Imaging Materials Science
Physical mechanisms and processes

A lecture series workshop - phy490

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Topics Outline

1. Conventional materials and processes
    - i. The photographic emulsion
        - a) Gelatin
        - b) Silver halides
        - c) Emulsion manufacture
    - ii. The formation of the latent image
        - a) The characteristic curve
        - b) The quantum model
        - c) Crystal structures
        - d) Semi-conductance and photoconductivity
        - e) The Gurney-Mott theory
    - iii. Mechanism of development

Topics Outline cont'd

2. Semi-conductance

   i. Energy bands

   - Valence bands, conduction bands, energy gap
   - Intrinsic and extrinsic semiconductors
   - N-type and p-type dynamics and Fermi levels
   - Energy diagrams
   - p-n junctions
   - The case of silicon

   ii. The Metal-Oxide semi-conductor

   - Structure and p-n dynamics
   - Photon-electron production and charge transfer
   - Charge coupling

Topics Outline cont'd

3.The Photodiode Device

i. Structures CCDs and CMOSs
   a) Phase pulsed CCDs
   b) Surface and burried channel CCDs
   c) Single array and matrixed arrays
   d) Complementary metal oxide semiconducors (CMOS)
   e) CMOS Passive and Active designs
   f) CCD and CMOS architectures

ii. Performance Factors
   a) Quantum efficiency
   b) Front/back lit CCDs
   c) Charge transfer efficiency
   d) Dark Current
   e) Signal to Noise ratio
   f) Linearity

Topics Outline cont'd

4. Image sensor implementations
    i. CCD vs CMOS charcteristics
    ii. Color Rendition
        - The Bayer Matrix, Demosaicing and Interpolation
        - The Layered approach: The Foveon X3 sensor
        - Beam Splitting and the 3 CCD assembly

5. Future of Imaging Materials

The Photographic Emulsion

Gelatin

Requirements:

- Keep Ag halide grains well dispersed and in suspension
- Must be relatively stable
- Developer penetration must be rapid
- Cheap and readily accessible
- Durable
- Enhances the sensitivity of Ag grains
- Must be transparent

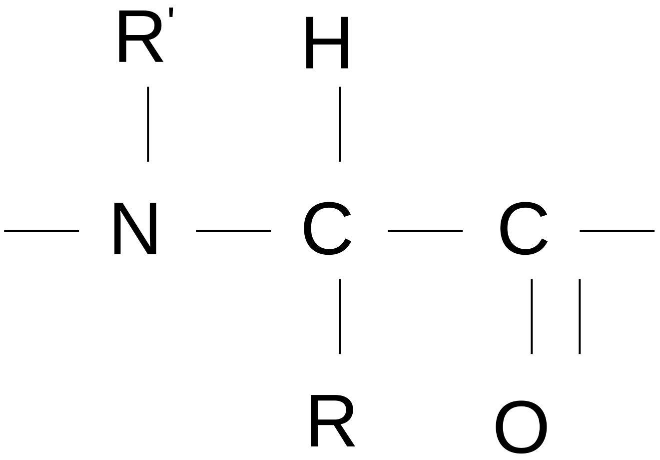
Origins: Calf hide, ear and cheek, southern cows fed with hemp are especially useful, product must be bacteria free

The Photographic Emulsion

Gelatin continued

Chemical composition:

- A protein
- Molecules are amino acid residues joined end to end to form long chains (peptide bonds), the chains are polypeptide chains.
- Typical amino acid residue is:



$$-\overset{\overset{R'}{|}}{N}-\overset{\overset{H}{|}}{\underset{\underset{R}{|}}{C}}-\underset{\underset{O}{\|}}{C}-$$

The Photographic Emulsion

Gelatin continued

Chemical properties:

Because of the NH_2 and COOH structure of the molecule it is both acidic and basic ie. amphoteric.

* In solutions with high hydrogen ion Content the NH_2 group transforms to NH_3+ therefore in an acid medium the Gelatin has a positive charge

* In a low hydrogen ion solution The COOH groups ionize to COO^- therefore the gelatin in basic Mediums has a negative charge

At some intermediate concentration of H+ ions the Gelatin has no charge, this defines the iso-electric pt. ie. the iso-electric point of gelatine lies in the range Of pH 4.7 to 5.2

Many of the physical properties of gelatin such as soluability, osmotic pressure and the degree Of swelling vary with pH and have their minimum value at the iso-electric point.

The Photographic Emulsion

Gelatin continued

Hardening:

- The emulsion can be hardened by having the amino group of the amino acid react with formaldehyde (CH_2O)

----------> $R\text{-}NH_2 + CH_2O \rightarrow R\text{-}NH{=}CH_2 + H_2O$

  – The methyline cross linkage 'weld' the emulsion together

Silver and the Halides
The Quantum Models

Silver, Ag, atomic# 47

47 protons, 47, neutrons, 47 electrons

Quantum levels:

$1s^2$

$2s^2, 2p^6$

$3s^2, 3p^6, 3d^{10}$

$4s^2, 4p^6, 4d^{10}, 5s^1$

Bromine, Br, atomic# 35

35 protons, 35, neutrons, 35 electrons

Quantum Levels:

$1s^2$

$2s^2, 2p^6$

$3s^2, 3p^6, 3d^{10}$

$4s^2, 4p^5$

The valence shell: ion with shared electron
Ag^+ ---------------------------- Br^-
Ag^+Br^- is the silver salt (silver bromide, ionic compound, first ionization potential = 7.542 eV)

The Silver Halides

- Silver halide comprises 30 to 40% of the emulsion weight
- Silver chloride and bromide crystals are arranged in a symmetrical structure – each ion is surrounded in space by six of the other ion
- Growth of silver halides crystals:
  - Crystals grow in layers with alternating silver or halide being added on.
  - Two types of crystals can be formed:a) octahedral (8 sides) or b) cubic (6 sides)
  - Crystals grow relative to: 1) presence of impurities, 2) excess of one or other ion
  - Cubic faces are produced when silver nitrate ($AgNO_3$) and potassium bromide (KBr) are mixed so that there is an equal proportion of Ag^+ and Br^- ions in solution.

Silver Halides cont'd

Size of grains:

- Growth of up to 20 µm is possible, in practice the largest are usually about 5 µm.
- Grain size will vary depending on the type of emulsion (fast or slow). Tabular grain engineering has changed the traditional size vs speed vs 'graininess' relationship
- Most grains are approximately 0.2 to 0.5 µm in diameter

It is important to consider the grains as individuals in the photographic emulsion because grains act as individuals in the photographic process

Concept of grain individuality in photographic emulsions

Each grain is an *independent* unit for latent image formation.

Emulsions exhibit a wide range of grain sizes and this variation is of considerable practical importance:

- Variation represented in terms of a size-frequency curve
- Larger grains absorb more light and are on the average more sensitive than the smaller ones, ie. They become developable at a lower exposure
- Emulsions covering a wide range of grain sizes should have greater range of light response (latitude) than grains containing only a small range.
- Size is not the only determinant in emulsion sensitivity.

Emulsion Manufacturing

- Silver halide is precipitated in a dilute gelatin solution
- The precipitate is allowed to 'ripen' ie. The grains are allowed to grow to the desired size
- When the precipitate is ripened, additional gelatin is added to set a firm gel – this is the *gelatin stage*
- The set emulsion is shredded and washed to free it of soluable salts
- Emulsion is then melted, fresh gelatin added and kept a a carefully controlled temperature
- The emulsion is finally coated on the film base

Stages in Emulsion Manufacture

Precipitation

- When silver nitrate is added to a soluable solution such as potassium bromide, a slightly soluable silver halide is formed and separates. The chemical reaction is:

$AgNO_3$ + KBr ----> AgBr + KNO_3

- Excesses in either one of the reactants will produce a charged ion and is an important factor in keeping the particles in suspension solution.
- Concentrated solutions of silver nitrate are necessary in preparations
- A protective colloid must be used to to prevent particles from coalescing in a curdy mess; the gelatin serves this function
- The method of mixing the component solutions is important (see text p.28)
- Larger quantities of gelatin during the precipitation ensures smaller grain size
- Therefore: Grain size is related to: a) time of precipitation, b) amount of gelatin, c)concentration of $AgNO_3$ + KBr
- High speed emulsions contain AgI, a small addition will significantly increase speed (to a max)
- Iodide exerts an influence in the size and shape of the grains (see graph, p.30)

Stages in Emulsion Manufacture

Ripening

Grains attain their final size and form, Increase in practical size at this point follows one of two pathways:

- Coalescence of two or more individuals, clumping together and recrystallizing to one well unified crystal
- Ostwald Ripening: being more important the larger grains grow at the expense of the smaller ones due to a difference in soluability. Basis for this process is in energy considerations (p.31)

- Rate of physical ripening depends on the concentration and the nature of the gelatin present
- One gelatin may accelerate at one concentration and restrain at another
- Impurities in the gelatin may also restrain ripening
- The gelatin's molecules may also promote grain growth but this is dependent on pH
- A mild silver halide solvent will increase the ripening rate (p.32) (bromide ion, ammonia)
- Temperature will also increase the ripening rate.

Stages in Emulsion Manufacture

Ripening

At the conclusion of the ripening stage the emulsion contains soluable alkali, ammonium nitrate, excess soluable halide, and ammonia (for ammonia emulsions)

- Problems:
    - Alkali will tend to crystallize upon drying
    - Ammonia will cause excessive fog
    - Excess soluable halide will decrease film sensitivity
- Washing the emulsion removes such substances and problems
- Procedure:
    - Emulsion is shredded into noodles
    - Noodles are washed until the excess bromide is reduced to the amount desired

Stages in Emulsion Manufacture

After-Ripening (Chemical sensitization)

Emulsion is melted and temperature is maintained at about 50°C for approx. 1hr.

No change occurs to the grain sizes (size or form)

There is an increase in sensitivity and contrast brought about by a chemical sensitizing action.

Chemical sensitizing:

- Can be produced by gelatin but the behaviour is dependent on gelatin type (compounds in gelatin promote activity)
- Sensitizing in active gelatin – allyl thiourea- in commercial gelatins - thiosulfate.

Stages in Emulsion Manufacture

After-Ripening (Chemical sensitization, con'd)

Sensitizer Groups:

- Compounds reacting with silver halide to form silver sulfide (sulfer sensitizers)
- Compounds reacting with reduced Ag+ to Ag^0 (reduction of silver sensitizers)
- Salts of gold and certain other noble metals

Concentration of sensitizers is very low (eg. one part allyl thiourea to 1M parts emulsion can produce a change in sensitivity)

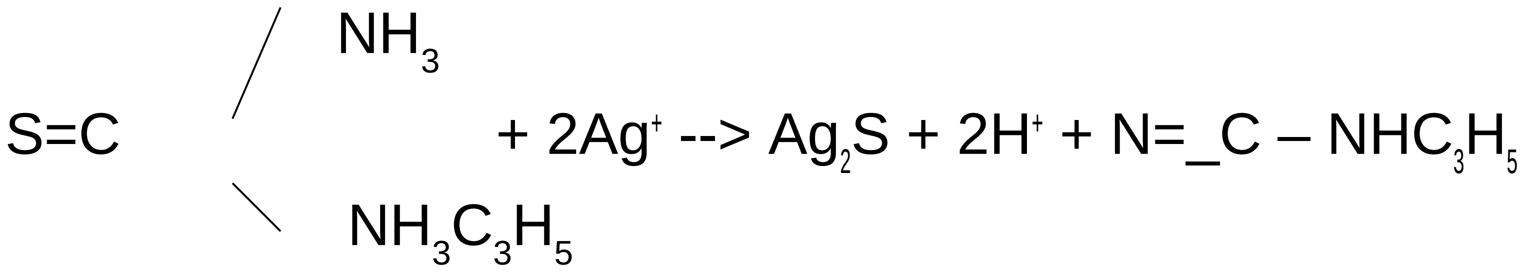
Large concentrations produce excessive fog.

Stages in Emulsion Manufacture

Chemical sensitization, mechanisms

Group I

Thioureas are strongly adsorbed by the AgBr, the reaction takes place on the grain surface: silver sulfide is formed.



$$S=C\begin{matrix} NH_3 \\ \\ NH_3C_3H_5 \end{matrix} \quad + 2Ag^+ \text{ --> } Ag_2S + 2H^+ + N=\_C - NHC_3H_5$$

Factors:

- Increase in temp. will increase reaction and sensitivity
- Increase in pH will increase reaction and sensitivity
- Decrease in halide ion will increase reaction and sensitivity
- Ag_2S catalyzes the reaction between Ag+ and thiourea

Stages in Emulsion Manufacture

Chemical sensitization, mechanisms

Group II

Reducing agents such as hydrazine act as sensitizers. These agents react with silver ions to form silver atoms. The Ag atoms appear to be responsible for increased sensitivity (Silver sensitizers)

Group III

Action of the gold compounds and gold ion complexes increase sensitivity

Ainous thiocynate can increase sensitivity well beyond sulfur sensitizers or silver sensitizers by formation of gold atoms on the grain surface.

Stages in Emulsion Manufacture

Final additions and coating

Enabling the emulsion to cope with mechanical stress during developing, fixing, washing with the addition of hardening agents – chrome alum.

-pH environment before coating can benefit overall sensitivity

Addition of dyes called *optical sensitizers* to extend emulsion sensitivity beyond 490nm (panchromatic, orthochromatic, infrared)

Coating:

- Suitable supporting material needed – glass, paper, cellulose acetate
- Typical compositions of finished photo emulsions vary in silver halide, gelatin, emulsion thickness
- For film: 60% gelatin, 40% Ag halide, ~1.5 mg silver halide/cm^2

Formation of the Latent Image

Latent Image Theory:

Two separate branches:

- **Statistical.** The statistical relationship between the developed density and the amount of exposure. This branch is essentially the theory of the origins of the characteristic curve.
- **Quantum Mechanics.** Investigates the actual mechanism of latent image formation in the individual silver halide grains

Formation of the Latent Image

Statistical – the characteristic curve

The characteristic curve: The origins

- The curve is obtained by plotting the developed optical densities against the logarithm of exposure
- The variation in density is caused by the *number of grains* developed per unit area
- At any point below the maximum density only a fraction of the grains are developed.
- The curve can be represented by a 9th order polynomial

Two view points exist on the relation between exposure and the number of developed grains

- Same size grains all have the same inherent sensitivity
- Individual grains vary widely in sensitivity and therefore the number of quanta (incident) to make the grain 'developable' differs from grain to grain

Formation of the Latent Image

Statistical – the characteristic curve

First view point:

If grains were all of the same sensitivity then the change in number of developable grains will change with the incident or absorption of light quanta hitting the emulsion.

- The number of times a grain is hit during a given exposure varies according to probability

Defining the variables:

- Suppose grains are of equal size
- N = number of grains per unit area
- Grains are in a single layer (none are shielding)
- Layer is exposed to uniform light (although light is uniform, at the atomic level light behaves randomly)
- S = Total number of quanta striking grains

Formation of the Latent Image

Statistical – the characteristic curve

Defining the relationship between quanta and grains struck or that are developable:

- The probability that any one grain will be struck by at least one quanta or photon will be
  - $1 - e^{-S/N}$ where:
  - $1 - x$ is the probabliity term
  - -S/N is the ratio photons to grains
  - e is the natural process logarithm
- This is the fractional number of grains struck by at least one quantum
- If one photon is sufficient to make the grain developable then the total number of developable grains (K) is:
  - $K = N(1 - e^{-S/N})$
  - $D = D_{max}(1 - e^{-E/Dmax})$, the optical density form.

Formation of the Latent Image

Statistical – the characteristic curve

An example:

$K = N(1 - e^{-S/N})$

Consider also the Planck-Einstien equation for describing quantum energy:

$E = h\nu$ or $E = hc/\lambda$,

where h = is the Planck constant

ν = the wave frequency, also $\nu = c/\lambda$ where

c = the speed of light, and

λ = the wavelength

If $S = E = 100h\nu$ and N = 500 grains of AgBr, solving for K:

$K = 500(.282) = 150$

The probability of a grain being hit is 0.282, 150 of the 500 grains are hit or made developable.

Formation of the Latent Image

Statistical – the characteristic curve

The second viewpoint:

- Assumes that the inherent sensitivities vary widely. The distribution of sensitivities is treated as a statistical problem.
- (Webb) treatment incident quanta varies from a few sensitive grains to several hundred.
- Transfer from developed grains per unit area to optical densities is made by a suitable factor
  - $D = A(K/N)$, where
    - A is a suitable factor
    - K is the # of grains (exposed)
    - N is the total # of grains

Formation of the Latent Image
The quantum model

Quantum absorption by ionic crystals

- Only EMR which is absorbed can be effective in latent image formation. If no optical sensitizers are present the absorption by the silver halide crystal is restricted to blue and shorter wavelenghts.
- Heavy quantum flux of Ag+Br- or Ag+Cl- produces free silver and halogen:
  - Br- + hν --> Br + e, and
  - Ag^+ + e ---> Ag, where hν is the quantum energy (E)
- Direct identification of this reaction has not been achieved but factors point to Ag as the <u>latent image</u> material.
  - Chemical reactions of Ag and the latent image are the same, latent image is destroyed by strong oxidizing agents such as potassium persulfate and free halogen So is Ag

Formation of the Latent Image

The quantum model

Quantum absorption by ionic crystals, con't

- Where exposure is great enough to produce detectable amounts of Ag, a direct proportion is established between silver liberated and the # of quanta absorbed (the halogen should be removed)
    - Extrapolating to lower exposure the straight line passes through the origin confirming the fact that the latent image is silver
- The photolytic formation of Ag is accompanied by the formation of free halogen. If halogen is not removed it can recombine with Ag.
- In the above mentioned experiments a halogen acceptor is introduced to remove the halogen. When this is the case every quantum of light absorbed forms a silver atom (Quantum efficiency 'QE' = 1)In the presence of the halogen the QE is much less.

Formation of the Latent Image

Structural considerations

Latent image nuclei and development centres

- Photolytic silver by irradiation appears as discrete particles
- Development of exposed grains starts at discrete points on the grain surface; these development centres presumably coincide with the latent image centres reached by the developing agent.
- Distribution of development centres on a silver grain (partially developed) is *Poisson,* where n is the number of centres and bar-n is the average number over all grains:

$$P(n) = (n^{-n})(e^{\bar{n}}))/n!$$

eg. 8 centres on a grain, n=8, bar-n = 8 representing an average grain

- ➔ $P(n) = (8^{-8})(e^{-8})/8!$
- ➔ $P(n) = .14$

Formation of the Latent Image

Structural considerations

Concentration Speck Hypothesis

- Early work presumed sulfide to absorb light in the emulsion, however, it is the silver halide which absorbs light and not sulfide
- ***The function of the silver sulfide nuclei was to change the distribution of silver atoms formed by quantum action; Silver sulfide serves as concentration centres for photolytic silver while light can be absorbed over the whole grain but silver atoms are formed only at discrete points on the grain; the grain becomes developable when the centre has acquired a sufficient number of Ag atoms.***
- It should be noted that the structure and even the nature of the sensitivity specks or centres remains in doubt.

Formation of the Latent Image

Structural considerations cont'd

Physical Imperfections in Ionic Crystals

- Imperfections have figured in the cause of sensitivity and the formation of the latent image
- A latent image could not form in a perfect crystal
- Imperfections are of two kinds:
  - Lattice site irregularities or *point defects*
  - Irregularities over large distances such as *dislocations*

A. Point Defects arise from thermal vibrations which cause ionic displacement from regular lattice locations. Two kinds are noted:

- Shottky defects – when a pair of oppositely charged ions is missing from the normal lattice position. In Ag^+Br^- crystals this type of defect is negligible due to relatively low temperatures

Formation of the Latent Image
Structural considerations cont'd

Physical Imperfections in Ionic Crystals, cont'd

- Point defects cont'd
    - Frenkel defects – an ion which has moved out of its normal position into an *interstitial position* (in between other ions). At room temperature only Ag+ can move about due to the energy available (fig.pg.49)
        - The energy required to form an interstitial silver ion is 1.27eV. The movement of this ion leaves a vacated position in its former location (ie. A hole)
        - At higher temperatures more Frenkel defects are evident. These ions can easily move about in an applied electric field.
- ➔ The number of such defects is provided by:
- ➔ $n=N\exp(-E_v/kT)$, where k is the Boltzmann constant

Formation of the Latent Image

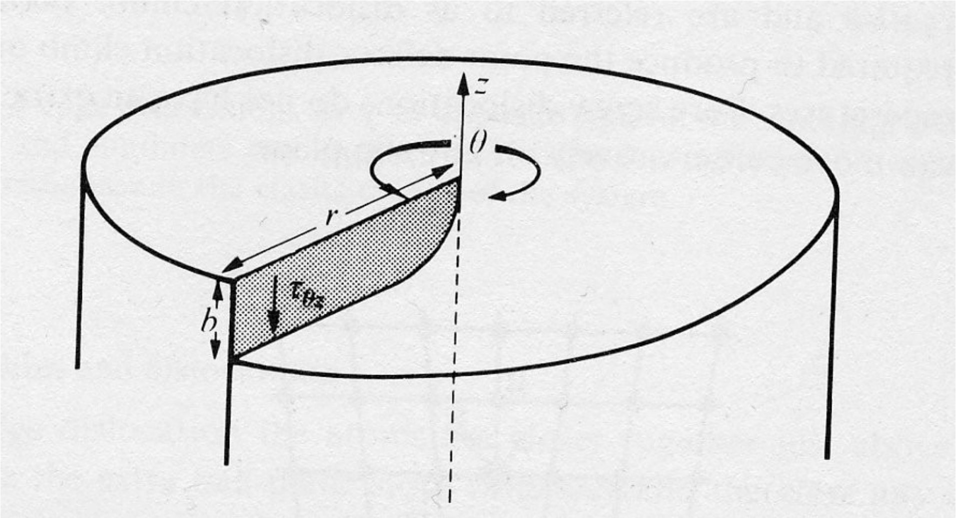
Structural considerations cont'd

Physical Imperfections in Ionic Crystals, cont'd

B. Dislocations (or Stacking Defaults): are line imperfections which extend for a relatively long distance within the crystal. Three types are recognized:

- Screw Locations – rotation around a centre point shows a helix type configuration:

Shear strain is: $\varepsilon_{\theta z} = b/2\pi r$, Shear stress is: $\tau_{\theta z} = Gb/2\pi r$, where b is the 'Burger vector' and G is the shear modulus



Formation of the Latent Image
Structural considerations cont'd

Physical Imperfections in Ionic Crystals, cont'd

B. Dislocations (or Stacking Defaults) cont'd

Edge dislocation – formed by an extra plane or pair of planes extending only part way through the crystal

Kink sites – surface distortions on ionic crystals (relevant to external as opposed to internal latent image formation

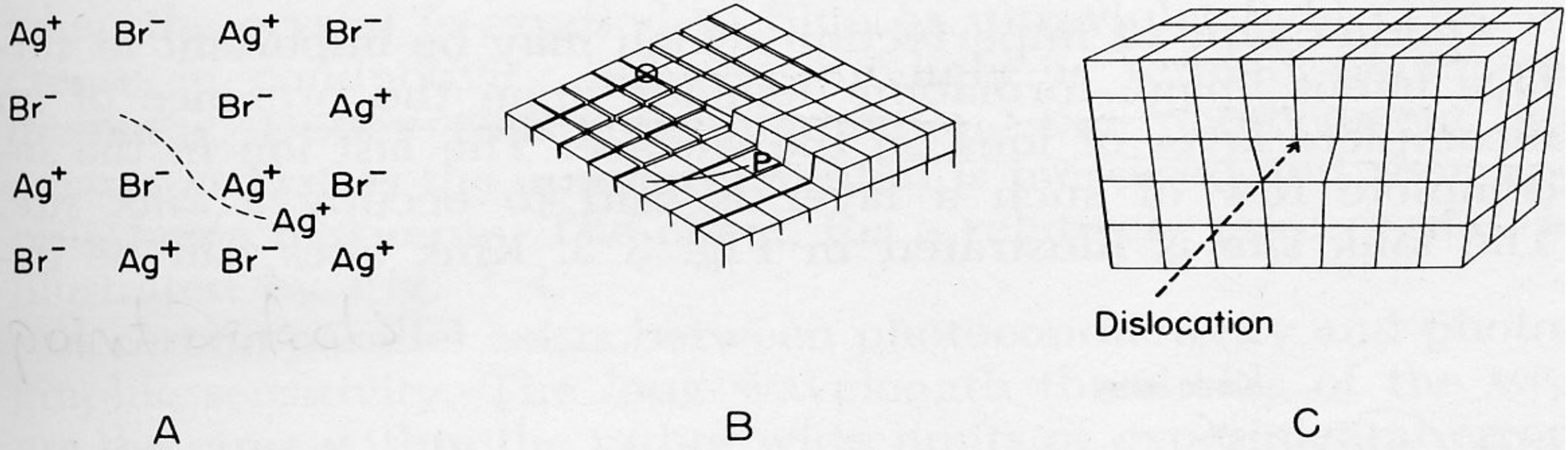


Fig. 3 · 2 A, Frenkel defect; B, screw dislocation; C, edge dislocation.

Formation of the Latent Image

Photoconductivity

Electrical Properties

- The electrical conductivity of Ag+Br- or Ag+Cl-, when a potential is placed across the crystals is low in in the dark; at room temperature it is 10^{-8}/ohm-cm fo Ag+Br-. Conductivity is increased when the crystal is exposed to blue or ultraviolet light. This increase is termed Photoconductivity.
- The mechanism of photoconductance is directly applicable to the mechanism of latent image formation.
- Photocurrent is produced by electrons moving through the crystal, conductance is directly proportional to the light intensity; therefore an increase in the number of quanta absorbed per unit time produces a corresponding increase in the number of photoelectrons which carry the current.
- Photoconductivity is best understood in term of the quantum mechanics of the crystal structure; the treatment relates the similarities and differences between photoconductance and normal metallic conductance

Formation of the Latent Image

Conductance and Photoconductivity

Energy of Free Electrons in Crystal Lattices

Energy states of valence electrons can be described by the wave function ψ

The wave function is described by Schrodinger's wave equation:

$$E\psi = -(h^2/2m)/(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2})$$

Where h is the reduced Planck's constant and m is mass (electron in our case)

As a standing wave , Schrodinger's equation reduces to:

$\Psi = A \sin k_x x \sin k_y y \sin k_z z$ where k is the wave vector and A is a constant

Also, remember that standing waves in a crystal are described by the wave vector $k^2 = k^2x + k^2y + k^2z = \pi^2 (n^2x + n^2y + n^2z)/L^2$ solid state p.85

The relation between energy (E) and the wave vector can therefore be obtained by substituting the k relationship above into Schrodinger's eq.

$$E(\psi) = h^2(k^2x + k^2y + k^2z)\psi/2m$$

And so.. $E = h^2k^2/2m$

Formation of the Latent Image

Conductance and Photoconductivity

Metallic Conductance

General Discussion:

- Electric current is carried by electrons moving through the crystal. These electrons occupy an energy band termed the *conductance band.* Which is only partially filled with electrons.
- Metals with uneven #'s of valence electrons only partially fill the uppermost occupied energy band.
- Metals with even #'s completely fill the band and may move into the second band with considerable freedom
- With Ag+Br- crystals the conductance band is normally completely empty and is separated from the highest filled band by a relatively large energy gap.
- Thus, an electron cannot acquire from thermal sources alone the energy needed to pass into the empty conductance band but the electron can obtain energy from the absorption of a light quantum of suitable λ

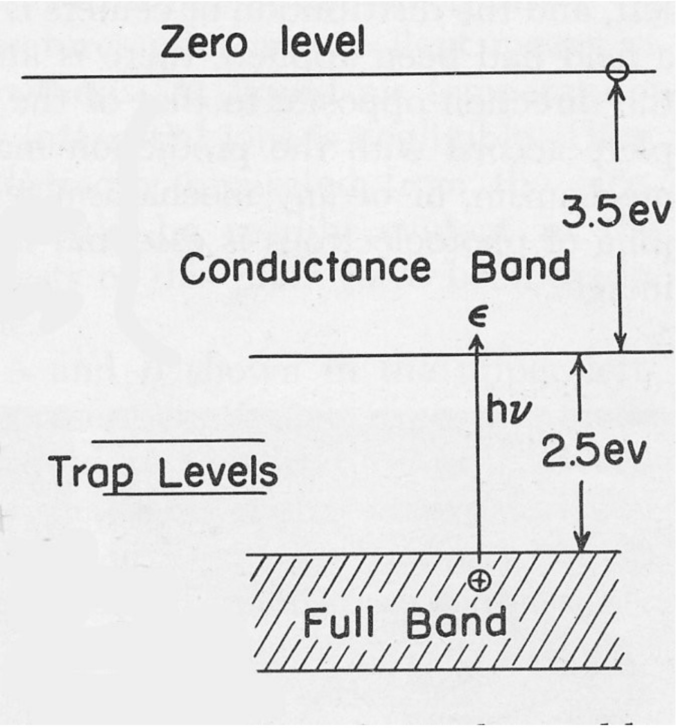
Formation of the Latent Image

Conductance and Photoconductivity

Metallic Conductance

General Discussion cont'd:

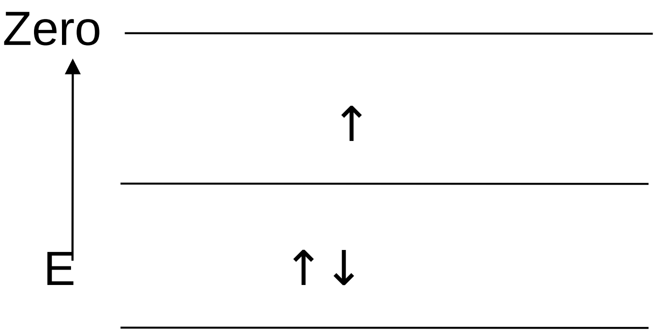
- A photo-electron thus liberated from a bromide ion can pass through the crystal with freedom comparable to that of a conductance electron in a metal crystal
- In Ag+Br- the full band is separated from the empty conductance band by an energy gap of approximately 2.5eV.
- The figure also shows a 'trap' energy level corresponding to impurities or a region of dislocation.
- An electron going from the conductance band to the trap level would lose energy and thus would need energy to move out of the energy trap --- it is for the time being trapped there.



Formation of the Latent Image

Conductance and Photoconductivity

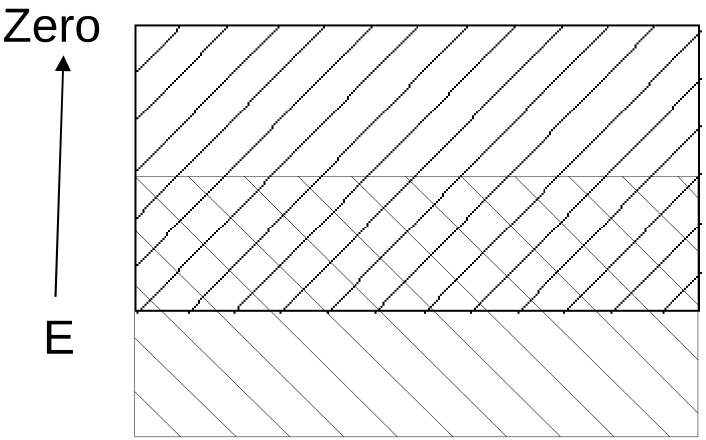
Conductance: a graphical illustration



Motion possible in conductance band (uppermost level)
(one electron in valence band)

Full band

1. Conductance when only one electron fills the valence shell, eg. Copper, iron..



Conductance band

Region of overlap -------> electron movement

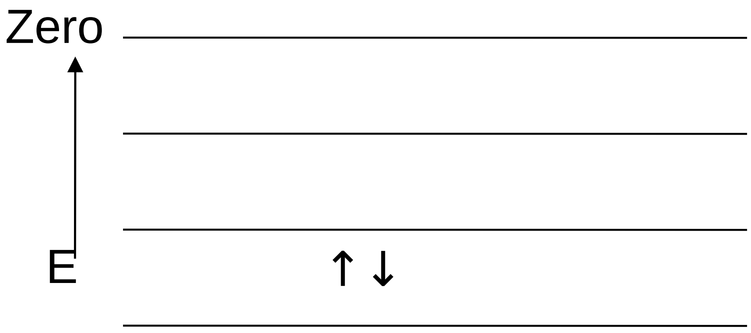
Full band

2. Conductance when two electrons occupy the valence shell, valence shell is full , however, Conductance is still possible due to the overlap of the conductance and filled bands eg. Mg, Ca

Formation of the Latent Image

Conductance and Photoconductivity

Conductance: a graphical illustration, cont'd



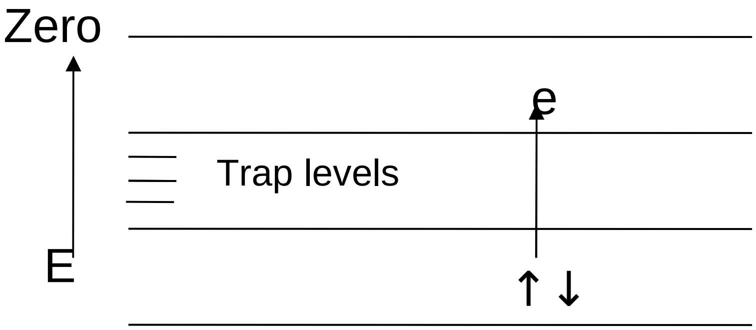
Conductance Band, no electrons

Energy Gap, width (or E) varies

Filled Band

3. Situation in which the valence shell is full and no electrons are in the conductance band. This Material would be an **Insulator**.

The silver bromide crystal quantum structure



Conductance Band, no electrons

Energy Gap = 2.5eV

Filled Band

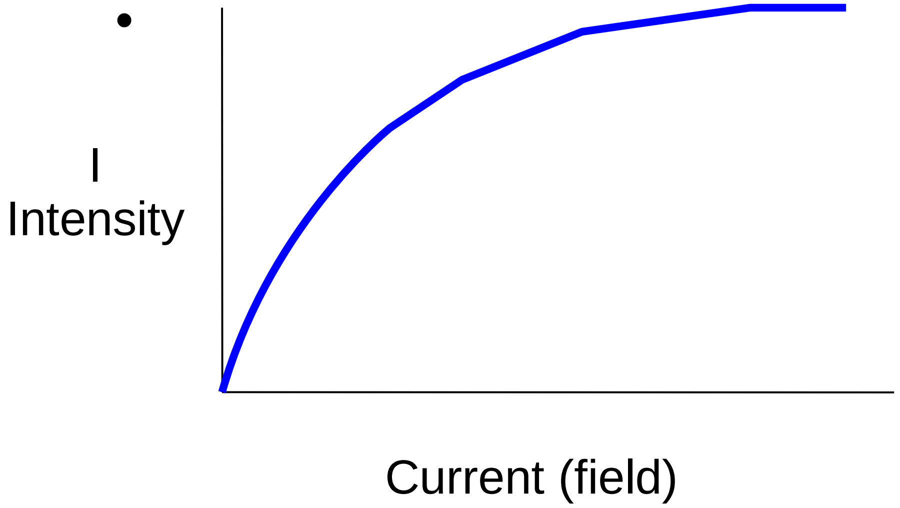
4. AgBr is normally an insulator. But when at least 2.5 eV Energy is absorbed by the crystal, Say, through a quanta of light, then it becomes a conductor ie. The valence electron is excited And moves to the conductance band.

Formation of the Latent Image

Conductance and Photoconductivity

Experimental evidence for AgBr photoconductivity

- Proof of mobility was demonstrated by applying a potential across an emulsion and looking at the formation of silver specks
    - Crystal with random sensitivity specks
    - Crystal with location of specks to positive electrode
    -



From Webb:
Photoconductance

Formation of the Latent Image

Conductance and Photoconductivity

Photoconductance applied: Webb's mechism

- Quantum of light is absorbed by the AgBr crystal
- Electron is transferred to the conductance band
- Electron has good mobility in this band
- If it enters a region of impurity or a structural fault it gets 'trapped' (losses energy). The impurities may be silver sulfide, the structural defects may be points or dislocations in the crystal.
- *An electron thus, can be trapped in an entirely different region of the crystal from where the quantum energy was absorbed.*

The latent image here is defined with electrons trapped at the sensitivity specks.

If the latent image involves movement by electrons as stated it should be possible to influence the location by applying an electric field: electrons would move opposite the direction of the applied field

Formation of the Latent Image

The Gurney-Mott Hypothesis

Latent Image Formation is twofold:

- Primary – An electronic process that is associated with photoconductance ie. Webb's mechanism
- Secondary – An ionic process involving the migration of interstitial Ag ions.

  – The electronic process is similar to Webb's mechanism – the electrons travel in the conductance band via their thermal energies.

  – Electrons trapped at the sensitivity centres (crystal imperfections or by impurities – silver sulfide - create an *electrostatic* potential. I Interstitial Ag+ ions are attracted to the negatively charged specks and migrate towards them. At the specks the ions are neutralized by the electrons and form Ag atoms.

Experiments at low temperatures confirm these theories.

Formation of the Latent Image

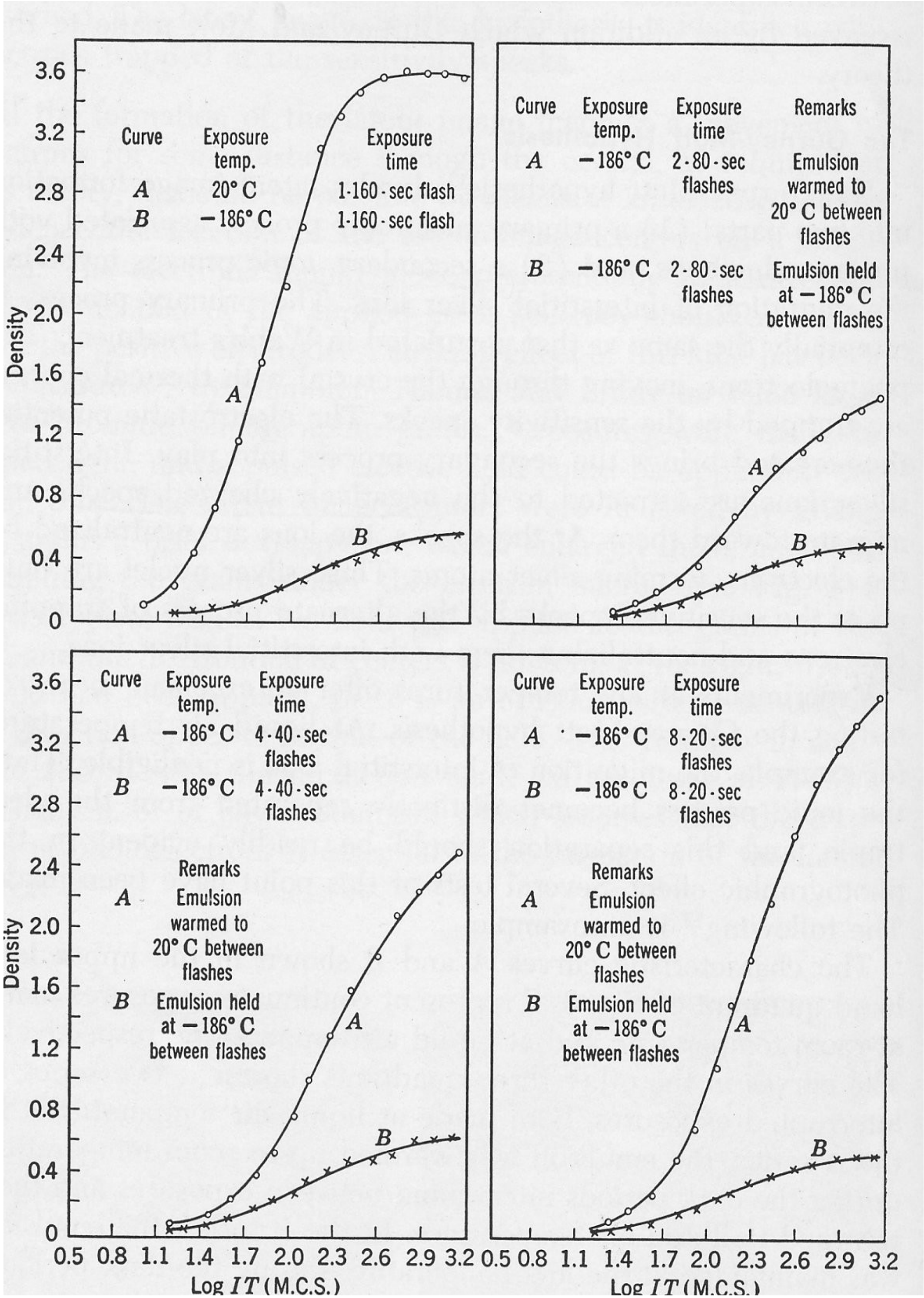
The Gurney-Mott Hypothesis, cont'd

- Implications of the G-M Theory suggest that when one electron is trapped but not neutralized at a given speck the approach of a second is hindered by the electrostatic repulsion.
- If an interstitial silver ion can move to the speck and neutralize it before a second electron approaches the latter will be captured. Otherwise the second electron will go elsewhere – to another trap or bromide atom.
- *The rate* at which a speck will collect silver deposits dependes on the *frequency* which both ions and electrons approach the speck: Consider a silver speck on the surface of a halide crystal. If the speck carries a charge of ne the field distance r from it will be ne/kr^2, where k is dielectric constant. Thus the total current due to the ions flowing towards it from all directions is:
  - ➔ $\pi n \sigma e/\kappa$, where σ is the electrolytic conductivity
  - ➔ The number of ions per unit time which is collected at the silver speck.

Formation of the Latent Image

The Gurney-Mott Hypothesis, cont'd

- At liquid air temperatures the charged specks (electrons) can be neutralized only at an extremely low rate; exposure is inefficient. Intermediate warm-up allows silver ions to move rapidly and neutralize the silver specks which then can trap additional electron upon the next exposure.



Formation of the Latent Image

Modifications of the Gurney-Mott Hypothesis

A. Nature of the Electron Traps

- The electron trap in the G-M mechanism is the silver sensitivity speck or silver nucleus. Experiments from melt do not support this, however. Photoconductance of grains with sulfur produces a significant decrease in photoconductance. Electron trapping by the silver sulfide may account for this.
- Matejec suggests sensitivity by specks are positively charged by adsorbed silver ions followed by an attraction of electrons, effectively reversing the order of the G-M hypothesis.
- The latent image, however, also forms inside the crystal whcih has been sulfur sensitized. The suggestion that dislocations, rather than impurities are primarily responsible as electron traps here (inside the grain)

Formation of the Latent Image

Modifications of the Gurney-Mott Hypothesis

B. Fate of the Halogen

- Not enough evidence is given by G-M Theory by the electrons going to the conductance band from the conductance ion
- Halogen atoms could recombine with electrons or attack photolitically formed silver, however, enough must survive or else no photograpic effect would be noticed.
- Halogen atom could be immobile in which case it could not attack from a distance but another movement could exist:
  - The halogen atom is surrounded by silver ions and the region has an excess positive charge. This region is termed a **positive hole**.
  - An electron can jump from a neighbouring halide to the halogen atom – In effect the ion and the atom change places, the region of positive charge moves to the the site of the new halogen atom.

Formation of the Latent Image

Modifications of the Gurney-Mott Hypothesis

B. Fate of the Halogen cont'd

- By a succession of electron jumps the positive hole (halogen) can move through the grain to the surface or until it becomes 'trapped'
- An objection is raised that the hole may move to a negatively charged sensitivity speck – Mitchel's mechanism accounts otherwise
- At the surface the halogen may react with a 'halogen acceptor' – gelatin, water, dyes, Ag, Ag_2S or Au have been suggested, although inconclusive evidence is presented at this point.

Formation of the Latent Image

Modifications of the Gurney-Mott Hypothesis

C. Other Actions of Sensitizing Centres:

- Ag, Ag_2S and Au may stabilize photolytic Ag thus increase sensitivity. Photolytic Ag is very unstable, decomposes in the ionic form in less than 1 second

D. Mitchel's Mechanism

This mechanism produces both electrons and interstitial silver ions but its occurrence at thermal equilibrium is negligible

- Positive holes are trapped before conductance electrons can be trapped
- Holes are trapped by surface halide ions at kink sites or molecules of silver sulfide or by other sensitizing impurities
- Bromide ion at kink site – positive will be trapped to form Br- ion, this is the stabilized by the passage of an Ag+ ion into an interstitial position
- Ag_2S – positive hole diffusing to the silver sufide molecule, an electron can pass from the sulfide ion to the positive hole leaving S- and one of the silver ions of the molecule passes into an interstitial position

Formation of the Latent Image

Modifications of the Gurney-Mott Hypothesis

Mitchell says that silver ions at kink and jog sites (edge locations) cannot trap a conduction electron at room temperature

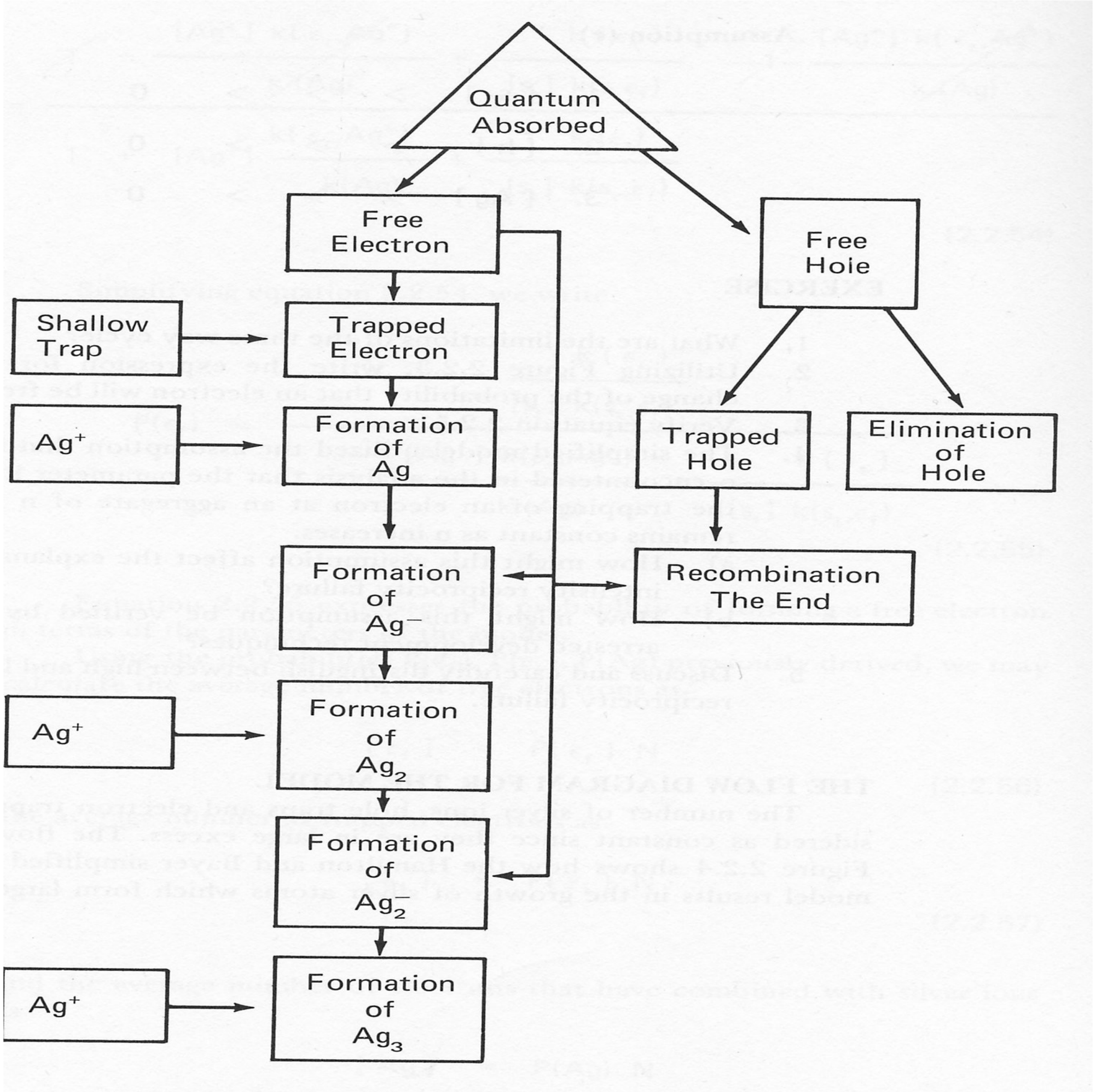
- If an interstitial silver ion is nearby, however, an electron can be drawn, to the space between it and the Ag+ ion at the kink; this will cause the two Ag+ ions to draw together to form Ag_2+ which is termed a latent pre-image speck.
- This Ag_2+ is not too stable and will dissociate into an interstitial Ag+ ion and conductance electron. But, if another interstitial Ag+ ion arrives it can combine with an electron and produce a pair of Ag atoms absorbed at the kink site. This is the latent sub-image speck
- A stable image is formed by recombination with a third interstitial ion and conduction electron.

Mitchel suggests that a group of 3Ag atoms can absorb a silver ion and become positively charged. This positive charge can attract other conduction electrons and rappel positive holes.

Formation of the Latent Image

Relating quanta, electrons, holes and Ag atoms

The question of how many photons are required to produce electrons that produce *developable* latent image silver is at the core of determining film's quantum efficiency and ultimate sensitivity. The crystal surface latent image process will be briefly outlined as outlined in the process diagram on the left.



Formation of the Latent Image

Relating quanta, electrons, holes and Ag atoms

The significant stages for a grain to form a latent image are:

1. Photon absorption stage (exposure)
2. The electron accumulation stage (semiconduction)
3. The nucleation stage (silver speck)
4. The growth stage

Each of these stages will be described briefly.

Photon Absorption: As a random statistical process quantum absorption will be associated with either the 1)Poisson or 2)Binomial probability distributions:

1) $$P(k, B_i, E) = \frac{(B_iE)^k)}{k!} e^{-B_iE}$$

2) $$P(A_i, E, k, \lambda) = \frac{(A_i, E)!}{k!(A_iE - k)!}$$

$$(\frac{\lambda}{A_iE})^k (1 - \frac{\lambda}{A_iE})^{A_iE-k}$$

Where: P = probability that a grain will absorb a photon, A=projected area of a grain E= Exposure (photons/cm2), λ=average # of photons absorbed, k=minimum number of photons Absorbed to render the grain developable, B=constant of absorption

Formation of the Latent Image

Relating quanta, electrons, holes and Ag atoms

Electron Accumulation: Two photon-created electrons must be accumulated in the grain to produce metallic silver. Success is measured by photon absorption (free electron) and hole removal. Failure is due to recombination (of the electron). The process, then, is a ratio of quantum successes and failures in the silver halide crystal:

Failure due to Recombination / Successful photon absorption:

$$\frac{NP(\epsilon_f)k(\epsilon_f, h_t)[h_t]}{Ik(h\nu, AgX)}$$

Failure due to recombination/ Successful hole removal:

$$\frac{NP(\epsilon_f)[h_t]k(\epsilon_f, h_t)}{[h_t]k(h_t)}$$

Where $P(\varepsilon_f)$=probability of a free electron, k=rate constant, h_t=trapped holes, I=exposure intensity, hν = quantum energy, AgX = silver halide, N=total number of electrons

Formation of the Latent Image

Relating quanta, electrons, holes and Ag atoms

Nucleation and Growth: A single silver atom is unstable due to recombination and at least two electrons producing two atoms of silver are required to produce a stable latent image centre. Fortunately, the single silver atom acquire a second silver ion and with a free electron arriving before the escape of this second silver ion, a stable 'speck' is formed. Growth is the enlargement of sub-image center until it becomes development center (at least 10 silver atoms). Again, the process is a ratio of successes and failures at the quantum level:

Failure due to recombination / Successful growth:

$$\frac{NP(\epsilon_f)[h_t]k(\epsilon_f, h_t)}{P(\epsilon_f)N[Ag_n]k(\epsilon_f, Ag)}$$

Where: terms are same as the previous formulation and Ag_n = the number of nuclei which have formed

The Mechanism of Development

General

Silver halide chemical development represents an amplification of sorts in making the latent image created during exposure visible. The process is one of a developer chemical being able to select those crystals that have been 'tagged' with photons (latent image silver specks) and convert them into silver metal ie. Ag^+ to Ag^0. Thus the basic reaction in development is the reduction of silver ions to silver.

The developer chemical reaction starts at those crystals that have latent image specks and proceeds to reduce the entire crystal. Note that the reaction is complete and the process is binary; photon affected silver halide crystals are either completely reduced to silver or not affected at all ie. The crystal grain is either black (developed) or white (not developed. As will be seen this is process is fundamentally different from silicon sensors where the number of photons used to create electrons can be some continuum and can be quantified by the bit rate.

The developer reaction is actually a rate process; the photonically tagged crystals are reduced to silver much more quickly than others. Thus the true action of the latent image silver is to accelerate (or catalyze) the actual reduction of silver ions.

The Mechanism of Development

The Charge Effect

The basic process for the reduction of Ag^+Br^- crystal is as follows:

1. The light exposed crystals are differentiated from the non-exposed crystals by the latent image silver specks
2. Those crystals need to have the developer (an electron donor) supply electrons to reduce all the Ag^+ ions to Ag^0 silver atoms.
3. The developer needs to be able to differentiate between those crystals with latent image silver specks and those without.
4. The charge effect is the mechanism that allows the developer to make this distinction and depends upon the fact that normal photographic emulsions contain an excess of negative halide ions and that these ions are adsorbed by the silver halide crystal
5. These emulsion halides create a negative charge barrier on the surface of the crystal and act to *repel* the developer electrons needed to reduce the silver ions
6. This charge barrier has the effect of 'insulating' all the crystals, <u>except</u> that those with silver specks (latent image) will have small areas on their surfaces where the charge is neutral (those with the Ag^0 silver atoms).
7. The developer uses these speck areas as 'points of entry' to reduce the complete crystal to metallic silver. The period required is the induction time.

Silicon as a semi-conductor

- Recall: An energy gap separates the valence band from the conductance band in semi conductors. Energy (thermal or quantum) is required to raise the energy state of the valence electron such that it will occupy the conductance band and be mobile under an applied potential.
- The most important semi-conducting elements are Germanium and Silicon. Eg silicon, atomic number 14:
    - $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$
- The valence band is completely filled ($3p^2$) and is separated from the conductance band by 1.1eV. This is the energy (E_g) required for a current to flow
- This results in mobile electrons in the conductance band and mobile holes in the valence band.

Investigating semi-conductance

Electron mobility: velocity (v) and acceleration (a)

- $v=h^{-1}\, dE/dk$

Recall that h is the modified Plank constant and that k is the wave vector (also described by the wave relationship $k=2\pi/\lambda$)

- $a=h^{-1}(d/dt)(dE/dk)$ (change in Energy with respect to the wave vector and time)
- $=h^{-1}(d/dt)(dk/dt)(dE/dk)$
- $=h^{-1}(dk/dt)(d^2E)(dk^2)$

- If an electric field is applied to the silicon there will be a force $-e\xi$ on the electrons; the electrons will accelerate and their energy state will change. So if the electron velocity is v the rate of energy absorption from an external field ξ is force X velocity. ie.
  - $-e\xi v = dE/dt = (dE/dk)(dk/dt)$, substituting for v: $-(e\xi/h)(dE/dk)$
  - $= (dE/dk)(dk/dt)$, hence: $-e\xi = h(dk/dt)$
  - Finally, substituting for dk/dt: $-e\xi=(h^2/(d^2E)(dk^2))a$

Investigating semi-conductance

Electron mobility: effective mass

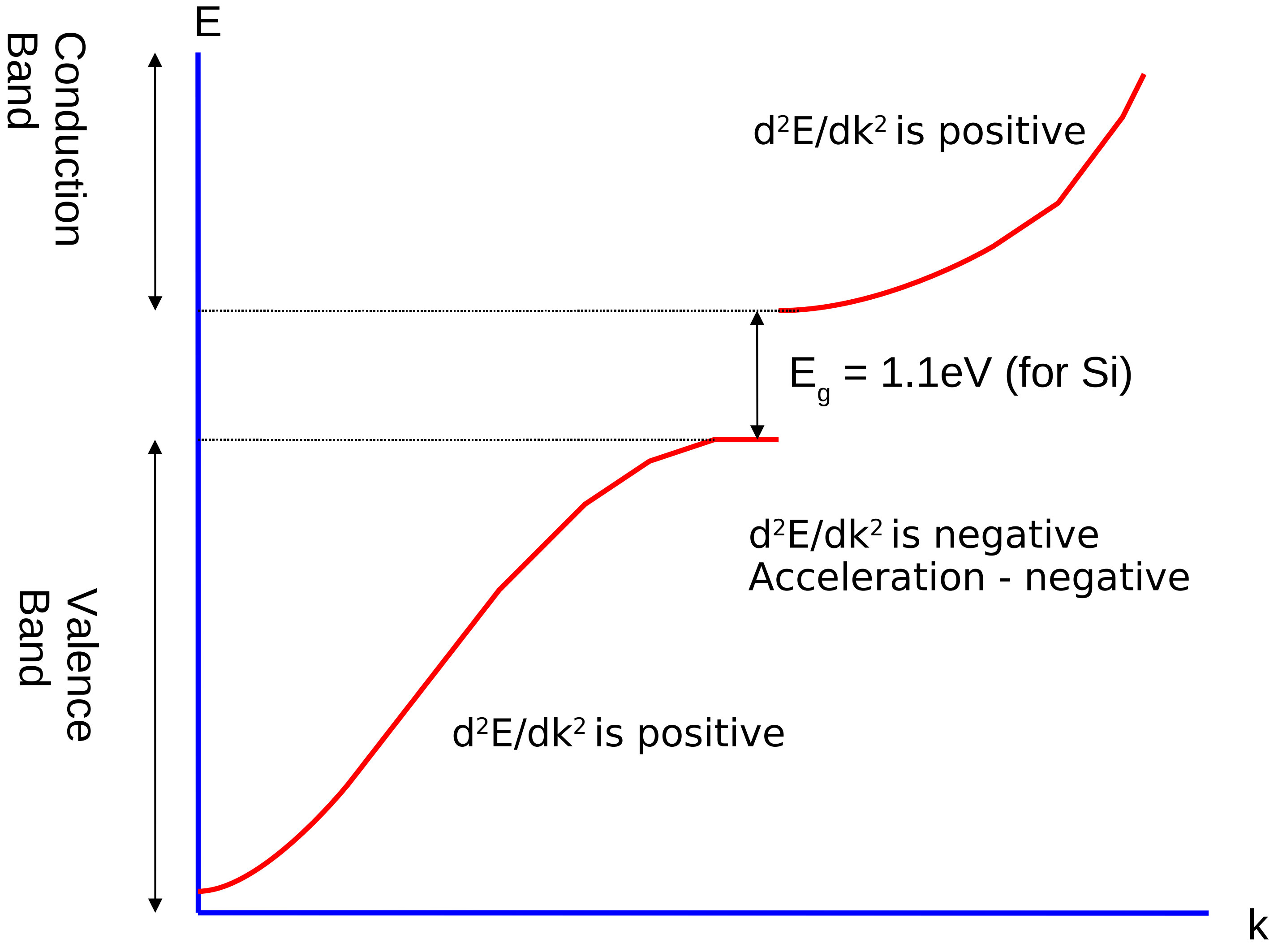
- $-e\xi=(h^2/(d^2E)(dk^2))a$

This is the relationship between the force on the electron *due to the external electric field* and its acceleration within the crystal. Using Newton's first law, $F=ma$ we can calculate the electron motion by only taking into account the external field, then $h^2/(d^2E)(dk^2)$ can be thought of the **effective mass of the electron.**

- Therefore, *if E varies as k^2 (or the square of the inverse of wavelength, or, as wavelength increases, E decreases), m will be constant*

- Note: As an electric field is applied the electron ***decelerates*** *as it approaches the energy gap boundary,* the momentum being exchanged with the lattice.

Investigating semi-conductance: a graphical representation



The relationship for positive k in fne dimension for a semiconductor

The electron velocity is proportional to the slope of the curve and tends to **Decrease** as the top of the first band is approached

Basic semi-conducting terminology

Intrinsic Semiconductors

- These are essentially pure semiconductors.The semiconductor material structure should contain no impurity atoms.
- For these semiconductors, as the temperature increases, the thermal energy of the valence electrons increases, allowing more of them to breach the energy gap into the conduction band.
- When an electron gains enough energy to escape the electrostatic attraction of its parent atom, it leaves behind a vacancy which may be filled be another electron. The vacancy produced can be thought of as a second carrier of positive charge. It is known as a ***hole*** (same as the silver halide lattice holes)
- If there are n free electrons in an intrinsic semiconductor, then there must also be n holes. Holes and electrons created in this way are known as intrinsic charge carriers. The carrier concentration or charge density defines the number of charge carriers per unit volume. This relationship can be expressed as n=p where n is the number of electrons and p the number of holes per unit volume.

Semi-conductor terminology cont'd

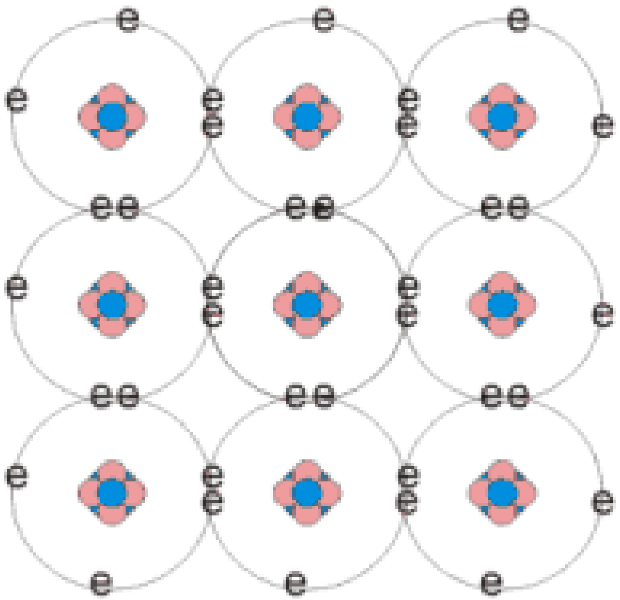
Extrinsic Semiconductors

- Formed from intrinsic semiconductors by added impurity atoms to the crystal in a process known as ***doping*. *E*** xample, consider Silicon, since Silicon belongs to group IV of the periodic table, it has four valence electrons. In the crystal form, each atom shares an electron with a neighbouring atom. In this state it is an intrinsic semiconductor. B, Al, In, Ga all have three electrons in the valence band. When a small proportion of these atoms, (less than 1 in 10^6), is incorporated into the crystal the dopant atom has an insufficient number of bonds to share bonds with the surrounding Silicon atoms. One of the Silicon atoms has a vacancy for an electron. It creates an a hole that contributes to the conduction process at all temperatures. Dopents that create holes in this manner are known as ***acceptors***.This type of extrinsic semiconductor is known as ***p-type*** as it create positive charge carriers. Elements that belong to group V of the periodic table such as As, P, Sb have an extra electron in the valence band. When added as a dopant to intrinsic Silicon, the dopant atom contributes an additional electron to the crystal. Dopants that add electrons to the crystal are known as ***donors*** and the semiconductor material is said to be ***n-type.***

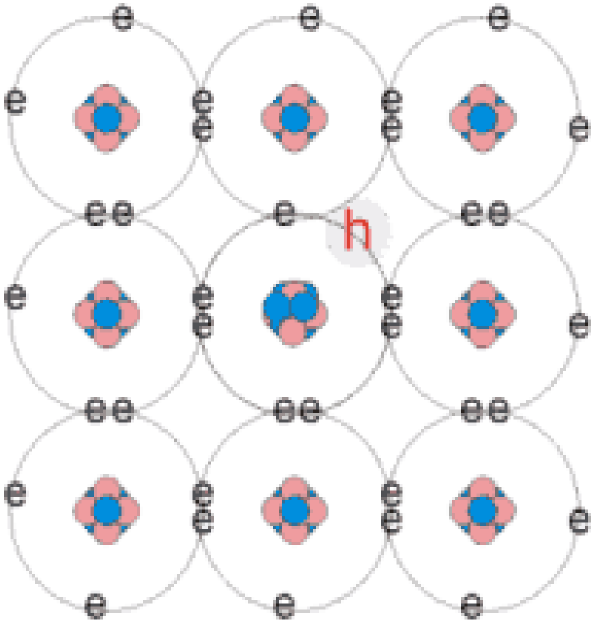
Semi-conductor terminology

n-type and p-type silicon

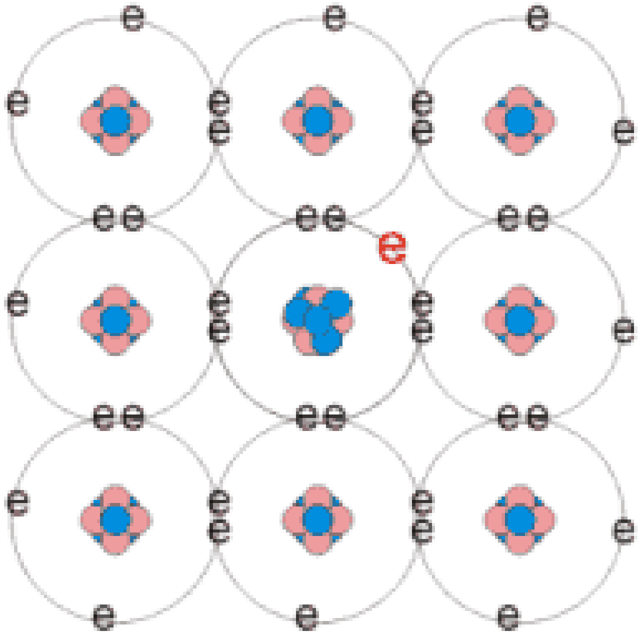
Semiconductor atomic structure diagrams



The intrinsic semiconductor



p-type extrinsic



n-type extrinsic

Semi-conductor physics

Semiconductors and the Fermi level

Electrons follow Fermi-Dirac Distribution function

$$f(E) = \frac{1}{Exp\left[(E-\mu)/k_B T\right]+1}$$

where μ is the Fermi Energy often denoted E_f or chemical potential in semiconductor physics is the energy at which there would be a fifty percent chance of finding an electron, if all energy levels were allowed. In order to apply the statistics, we need the density of states in the conduction and valence bands. These are derived from the basic principle that the density of states is constant in k-space.

In the conduction band the density of states is given by:

$$g(E) = \frac{V}{2\pi^2\hbar^3}\left(2m_e\right)^{3/2}\left(E-E_g\right)^{1/2}$$

and the valence band,

$$g(E) = \frac{V}{2\pi^2\hbar^3}\left(2m_h\right)^{3/2}\left(-E\right)^{1/2}$$

Semi-conductor physics

Intrinsic semiconductors and the Fermi level

The density of electrons in the conduction band is

$$n = \frac{N}{V} = \frac{1}{V}\int_{E_g}^{\infty} f(E)g(E)dE$$

$$= \frac{(2m_e)^{3/2}}{2\pi^2\hbar^3}\int e^{-(E-\mu)/k_bT}\left(E-E_f\right)^{1/2}dE$$

$$= 2\left(\frac{2\pi m_e k_b T}{\hbar^2}\right)^{3/2} e^{-(\mu-E_g)/k_bT}$$

In the valence band, the probability of a hole is $F_h(E) = 1 - F(E)$

and can be approximated $F_h(E) = e^{(E-\mu)/k_bT}$

A similar calculation yields the hole density

$$p = 2\left(\frac{2\pi m_h k_b T}{\hbar^2}\right)^{3/2} e^{-\mu/k_bT}$$

Semi-conductor physics

Intrinsic semiconductors and the Fermi level

Calculation of the Fermi level given the carrier concentration is useful in the calculation of laser gain, but since the function is not invertable, there is no analytical method for achieving this. However numerous approximations have been formulated to calculate the Fermi level.The value of μ depends on N_a and N_d . However μ can be eliminated (previous eq.) to give the important relation

$$np = n_i^2 = N_c N_v e^{-E_g/k_B T}$$

where N_c and N_v are the prefactors

$$N_c = 2\left(\frac{2\pi m_e k_b T}{\hbar^2}\right)^{3/2}$$

$$N_v = 2\left(\frac{2\pi m_h k_b T}{\hbar^2}\right)^{3/2}$$

As stated, np holds for all T and independent of the values of N_a and N_d . In the intrinsic region, the extrinsic density is negligible, and then n=p since each electron excited to the conduction band leaves a hole behind it. In the intrinsic region, therefore

$$n_i = p_i = \left(N_c N_v\right)^{1/2} e^{-E_g/2k_B T}$$

Semi-conductor physics

Intrinsic semiconductors and the Fermi level

Final formulation:

Given that

$$n_i = p_i = (N_c N_v)^{1/2} e^{-E_g/2k_bT}$$

and that we previously defined n as

$$= 2\left(\frac{2\pi m_e k_b T}{\hbar^2}\right)^{3/2} e^{-(\mu-E_g)/k_bT}$$

and p as

$$p = 2\left(\frac{2\pi m_h k_b T}{\hbar^2}\right)^{3/2} e^{-\mu/k_bT}$$

We can state the formulation for μ, the Fermi level as:

$$m_e^{3/2} e^{-(\mu-E_g)/k_bT} = m_h^{3/2} e^{-\mu/k_bT}$$

$$\mu = \frac{1}{2}E_g + \frac{3}{4}k_b T \ln\left(\frac{m_h}{m_e}\right)$$

Semi-conductor physics

Extrinsic semiconductors and the Fermi level

What happens to μ with temperature when donors and acceptors are present?
The charge neutrality condition governs the numbers of carriers.

$$n + N_a^- = p + N_d^+$$

where N_a - and N_d + are the number of ionised acceptor and donor sites. The number of sites that are ionised is:

$$N_d^+ = N_d\left[1 - f\left(E_g - E_d\right)\right]$$

A similar argument shows that

$$N_a^- = N_a f\left(E_a\right)$$

Semi-conducting physics

Extrinsic semiconductors and the Fermi level

We take the case of n-type doping but with some counter-doping:

$N_d > N_a$ and $N_a > 0$

at T=0, N a electrons move off donor sites to occupy the acceptor sites. Thus

$$N_d^+ = N_a$$

The donor sites are partially occupied. This is only possible at T=0 if the Fermi-level is at the donor-site energy:

$$\mu = E_g - E_d$$

his will not change for very low temperatures, $k_b T << E_d$, so substitution of the value of μ into the definition for n (intrinsic) gives

$$n = N_c e^{-E_d / k_b T}$$

Semi-conductor physics

Extrinsic semiconductors and the Fermi level

It is seen that $N_a^- = N_a f(E_a)$ is definitely a low-temperature result. For p-type doping, the result corresponding to $n = N_c e^{-E_d/k_bT}$ is: $p = N_v e^{-E_a/k_bT}$

The important technical region in the n-type material is the temperature range in which all the donors are ionised and the extrinsic electron density is higher than the intrinsic density. Full ionisation mean $n = N_d - N_a$

Since N $_a$ electrons are required for occupation of the acceptor sites.

$$\mu = E_g - k_bT\,ln\left(\frac{N_c}{N_d - N_a}\right)$$

, this is from $n_i = p_i = \left(N_c N_v\right)^{1/2} e^{-E_g/2k_bT}$ and

$$dk\frac{dk}{dt} = \lim_{\delta t \to 0}\frac{\delta k}{\delta t} = \frac{1}{\hbar v_g}\frac{\delta E}{\delta t} = -eE_f\frac{1}{\hbar v_g}\frac{dx}{dt}$$

The corresponding results for p-type doping are

$$p = N_a - N_d$$

$$\mu = E_g - k_bT\,ln\left(\frac{N_v}{N_a - N_d}\right)$$

Which simplify to:

$$n = N_d$$

$$p = N_a$$

Note that in this technical region the counter doping is negligible

Semi-conductor physics

n-type and p-type dynamics: a review

i. Determining number of charge of current carriers excited

ii. Determining the numbers of the various donor and acceptor states

iii. Position of the impurity levels within the energy gap

The two standard measurements are taken to determine these properties are the *electrical resistivity* and the *Hall coefficient*

The Hall resistivity allows determination of the density (N) of the carriers and their sign. If we know N and the resistivity ρ then the mobility μ may be calculated from a relation which is really a definition of the conductivity σ

$\sigma = 1/\rho = e\mu N$ *where e is the electronic charge.*

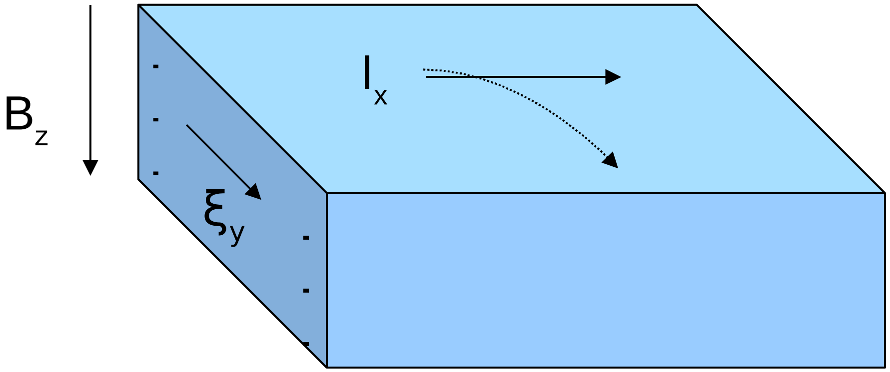
The mobility is the average drift velocity of the carriers in unit electric field

Semi-conducting physics

n-type and p-type semiconductor dynamics: a review

The Hall effect:

If a current flows along a conductor which is in a magnetic field whose direction is perpendicular to the direction of the current flow, then an emf (the Hall emf) is generated across the specimen in the direction which is perpendicular to to the magnetic field ie. The current, the magnetic field and the Hall emf are mutually perpendicular



The application of the magnetic field will cause the moving charges to deviate to the right side where a space charge will accumulate. This will produce an electric field which will eventually be sufficient to counteract the main magnetic field and prevent the deviation. The Hall effect is this secondary compensating magnetic field.

Semi-conducting physics

n-type and p-type semiconductor dynamics: a review

Following the from the previous slide:

The velocity of electrons is v_x in a magnetic field B_z and the Hall field is ξ_y, as the fields balance the force $\xi_y$must be equal to the opposite force B_z :

$E\xi_y = ev_xB_z = j_x\, B_z/N$ where $j_x = Nev_x$ is the current density

The Hall coefficient R_H can now be defined as:

$R_H = V_hz/(I_xB_z)$

Where I_x is the current through the specimen V_H is the measured Hall emf and z is the thickness of the specimen in the z direction. Since

$V_H = E_yy$ *and* $I_x = j_xyz$ then we obtain

$R_H = \xi_y/(j_xB_x) = 1/(Ne)$ -----------------------> **The Hall coefficient**

Semi-conducting physics

n-type and p-type semiconductor dynamics: a review

Excitation of carriers: the Fermi energy of an intrinsic semiconductor

Calculating the number of carriers N_e that are excited into the conduction band at a temperature T is described by 'carriers excited = density states X probability of occupation'

$$N_e = \int_{E_g}^{\infty} g(E) f_{FD}(E) dE$$

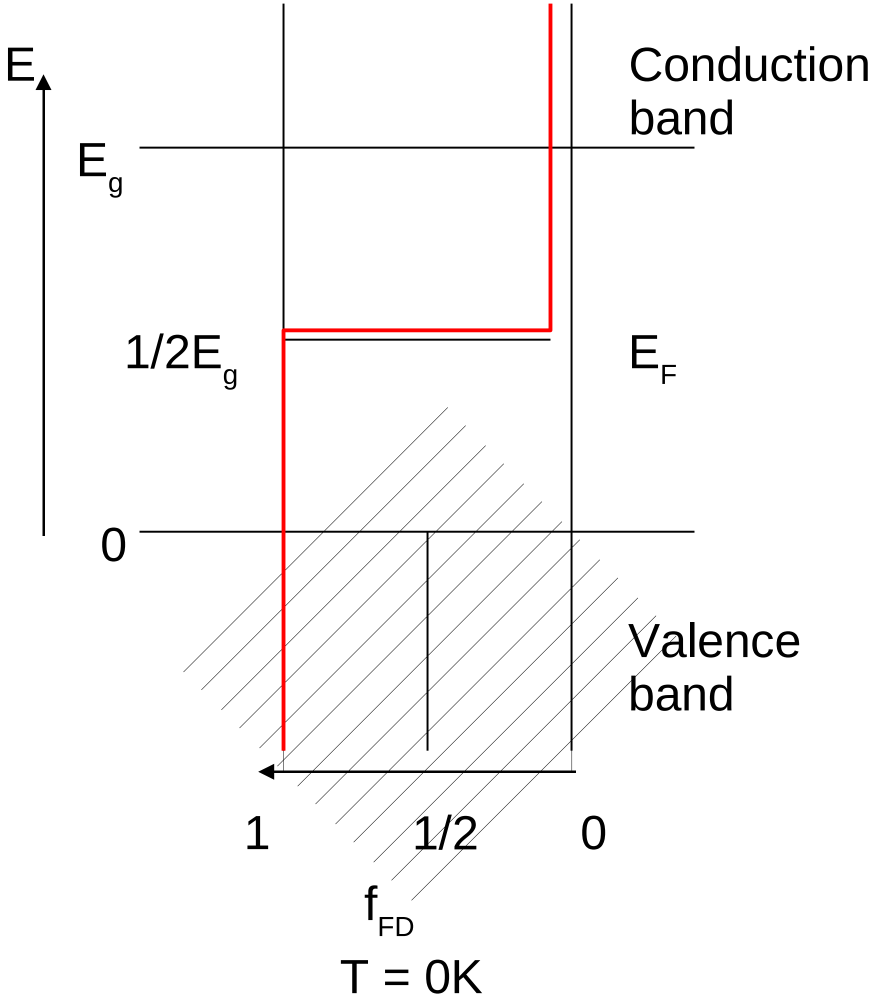
Where the top of the valence band is zero energy and E_g is the bottom of the conduction band.

The Fermi-Dirac function $f_{FD} = [\exp\{(E-E_F)/(kT)\}+1]^{-1}$ contains the parameter E_F which is the Fermi energy for metals and is equal to the energy of the highest occupied state at 0K, it does not change much at higher Ts. More generally this is the energy at which the probability of occupation is 0.5 or ½ E_g

Semi-conducting physics

Excitation of carriers: the Fermi energy of an intrinsic semiconductor

(at 0 K)



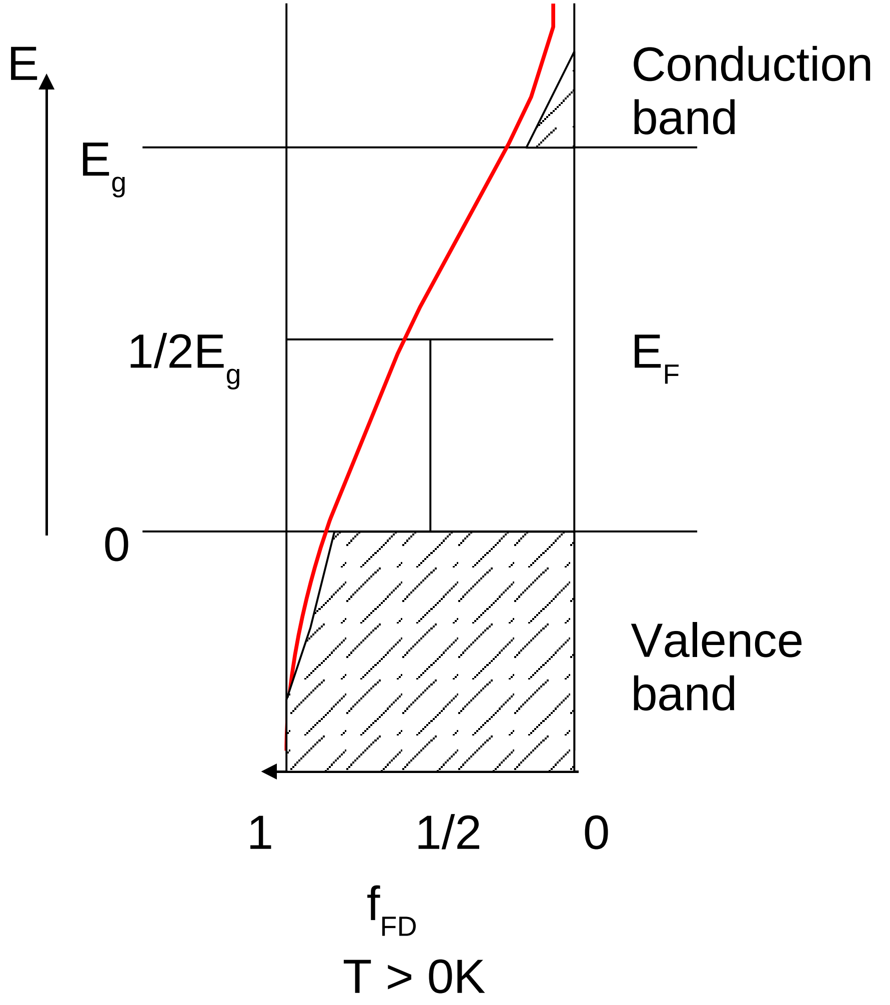
The valence band is full, the conduction band Empty. f_{FD} is a step function which must Therefore change its value from unity to 0 Within the energy gap and by symmetry it Seems reasonable that E_F should be at $1/2E_g$

Semi-conducting physics

Excitation of carriers: the Fermi energy of an intrinsic semiconductor

(at >0K)

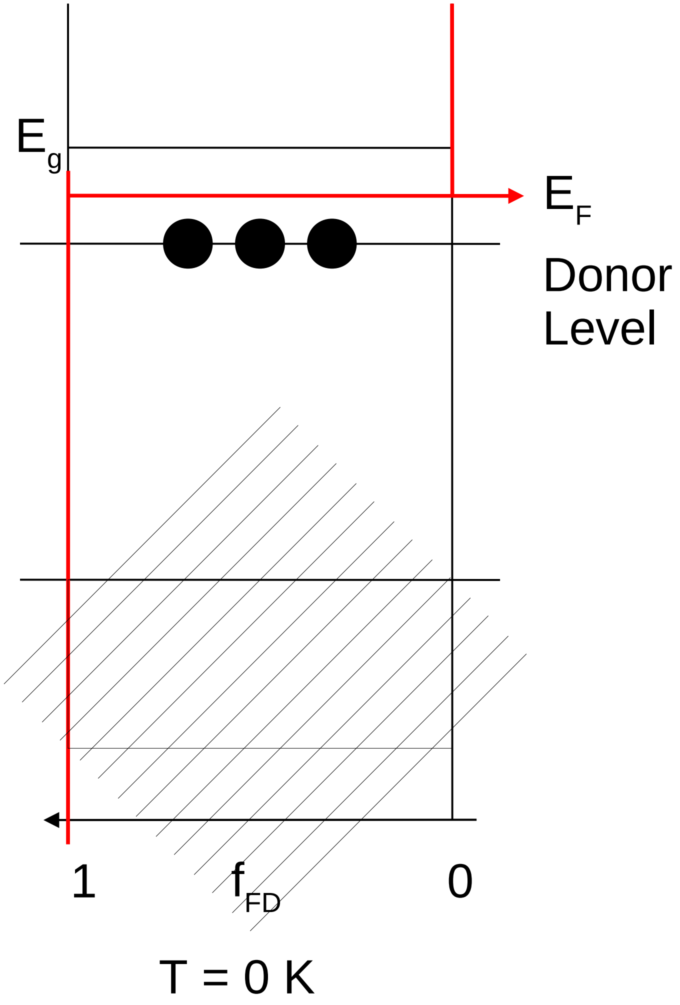
At higher temperatures there are
As many electrons excited into the
Conduction band as there are holes in
The valence band and so E_F remains
At $1/2E_g$



Semi-conducting physics

Excitation of carriers: the Fermi energy of an extrinsic semiconductor

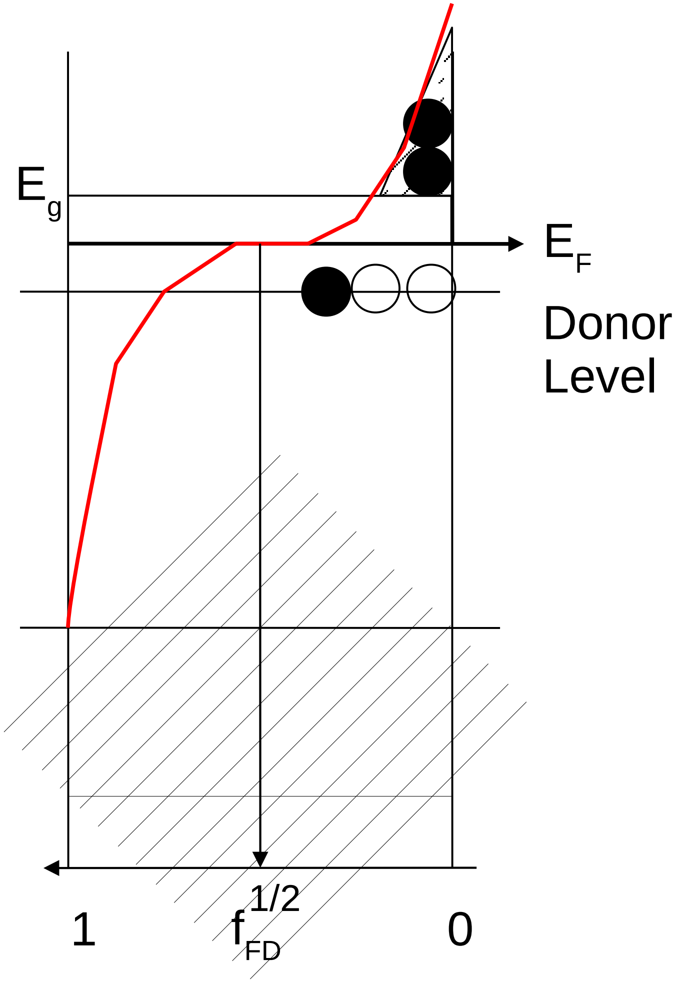
A doped specimen (at 0K)



The position of E_F for n- and p- type Specimens is quite different than for Intrinsic materials. Considering a n-Type sample (no acceptor impurities) All states up to and including the Donor level are occupied and the Conduction band is empty. E_F lies Therefore somewhere between the Donor level and the conduction band edge

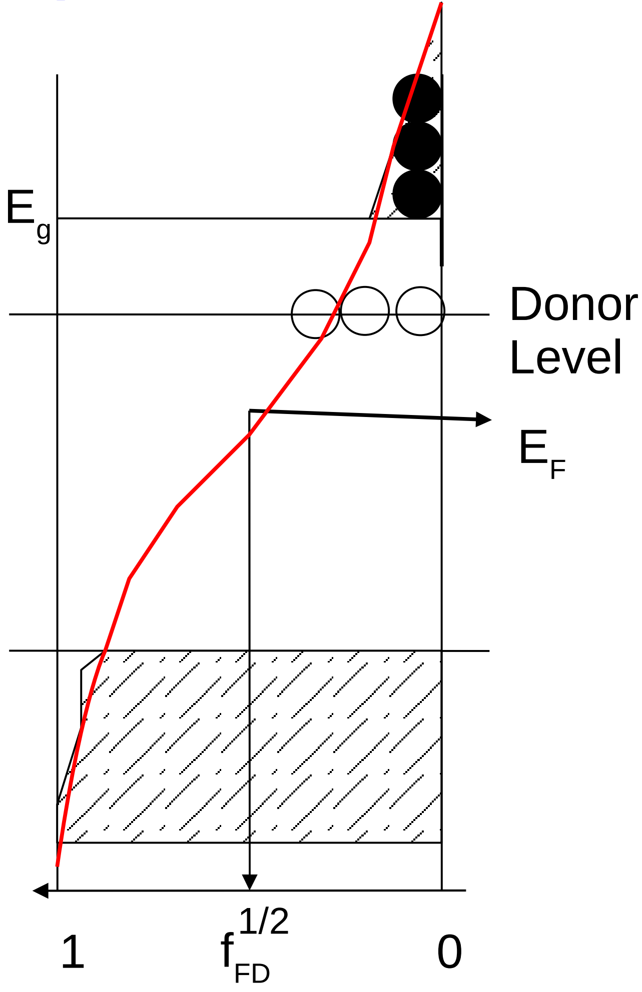
Semi-conducting physics

Excitation of carriers: the Fermi energy of an extrinsic semiconductor
A doped specimen (at T> 0K)



T > 0 K

As the temperature is
Increased E_F remains
in the region, falling
Slightly as more donors
Are ionized. It is only
At very high temperatures
When intrinsic excitation
Is so high that there are
Almost as many holes
Excited as there are
Electrons, that the
Probability for 50%
Occupation will be at
$1/2E_g$



T >> 0 K

Semi-conducting physics

Calculating the number of electron and holes in a semi-conductor

Deriving a useful relationship for the product of N_eN_h where N is the number of electrons and holes, respectively. First assume that $(E-E_F) > kT$, then we may approximate the Fermi function f_{FD} by $exp\ \{(E_F-E)/kT\}$ and we may write (see previous slides):

$$N_e = \int_{E_g}^{\infty} g_c(E) exp((E_F - E)/kT) dE$$

Where g_c is the density of states in the conduction band

Simplifying the equation by substituting $x=exp\ \{(E_F-E)/kT\}$:

$$N_e = \exp{(E_F - E_g)/kT} \int_0^{\infty} g_e'(x, T) exp(-x) dx$$

Similarly substituting $y=-E/kT$ in an expression for H_h (the probability of occupation of a hole is $1 - f_{FD}$):

$$N_h = \exp{(-E_F/kT)} \int_{-\infty}^{0} g_v'(y, T) exp(-y) dy$$

Therefore $N_eN_h = exp(-E_g/kT)$ X (function of T and the band shapes)

Semi-conducting physics

Calculating the number of electron and holes in a semi-conductor, concluding remarks

- $N_e N_h$ is independent of the Fermi Energy (E_F), thus it is constant at a given temperature for any semiconductor.
- It is independent of the amount of doping or whether it is a n- or p- type.
- For a heavily doped n-type semiconductor the concentration of holes will be very small
- For a heavily doped p-type semiconductor the electron numbers will be very small.
- For a pure semiconductor (no donor or acceptor levels), N_e must equal N_h and the relationship $N_e = N_h = constant\ X\ exp\{-E_g/(2kT)\}$ holds.
- At room temp. $N_e N_h$ is ~ $10^{33} m^{-6}$ for Si. So, if there is no doping $N_e = N_h$ is ~ $3X10^{16} m^{-3}$ for Si. This shows that in order to observe *intrinsic* behaviour in Silicon at room temp. any ionized impurities must contribute considerably less than $3X10^{16} m^{-3}$ carriers; in the order of 1 part in 10^{12}

Semi-conducting physics

The p-n junction

The junction formed when a p- semiconducting material is in contact with an n- type material has very remarkable properties and forms the basis of most semiconducting devices. It is based on two principles:

1. When two materials are in contact, charge transfer occurs until their Fermi energies are the same.
2. In n- and p- type materials E_F lies approximately at the donor and acceptor levels respectively

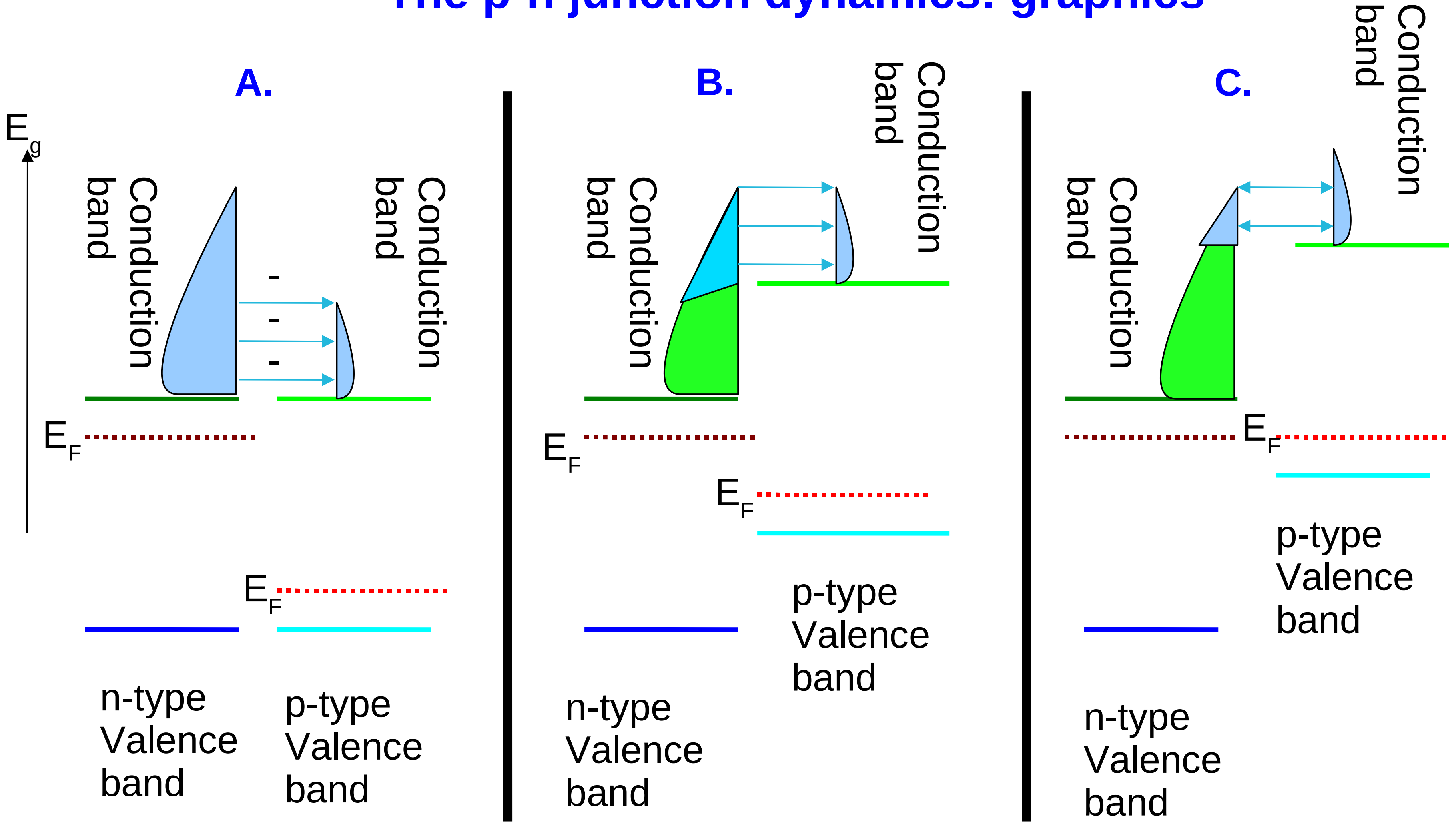
(a) Initially, when n- and p- type materials are placed in contact the excess electrons on the n- type side can reduce their energy by diffusing in to the empty states of the p-type material and thereby charging it negatively.

(b)The electric field produced will tend to oppose the further diffusion of electrons *or* the energy levels are displaced relative to one another.

(c) Eventually a dynamic equilibrium will be established at a point where the relative shift of the energy levels is such that transitions at *any* particular energy level are equal on either side of the junction. (see diagrams, next)

Semi-conducting physics

The p-n junction dynamics: graphics



A. Initially far more electrons diffuse from n- to p- than in the reverse direction. B. The net diffusion from n- to p- *charges* the p- negatively and there is a relative shift in energy levels. C. Finally equilibrium is achieved when the levels have shifted so that there equal transition of carriers at corresponsding energies on either side of the junction

Semi-conducting physics

The p-n junction: the depletion layer

The initial surge of electrons from the n- to p- materials and the resulting holes will create two regions of *donor* ions and *acceptor* ions, respectively. These would be two *depletion layers* containing fixed but opposite charges. They behave as a charged capacitor.

The amount of charge required to equalize the Fermi energy is small ie. Less than 10^6 electrons.

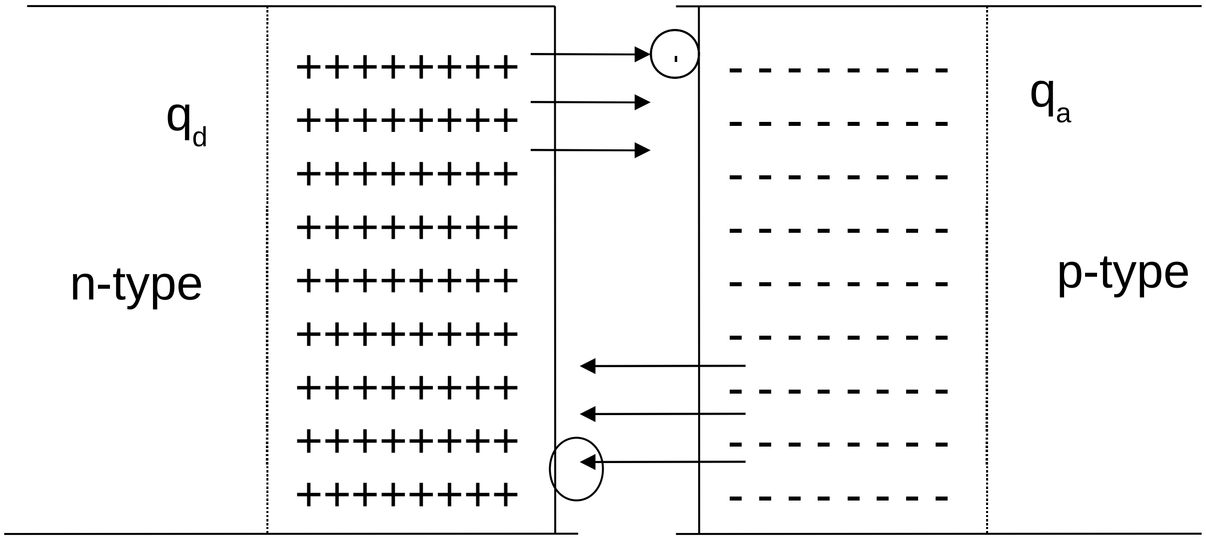
The effective width and capacity of the depletion layer is solved by Poisson's equation:

------------------------------> $d^2V/dx^2 = -\rho/\varepsilon\varepsilon_0$

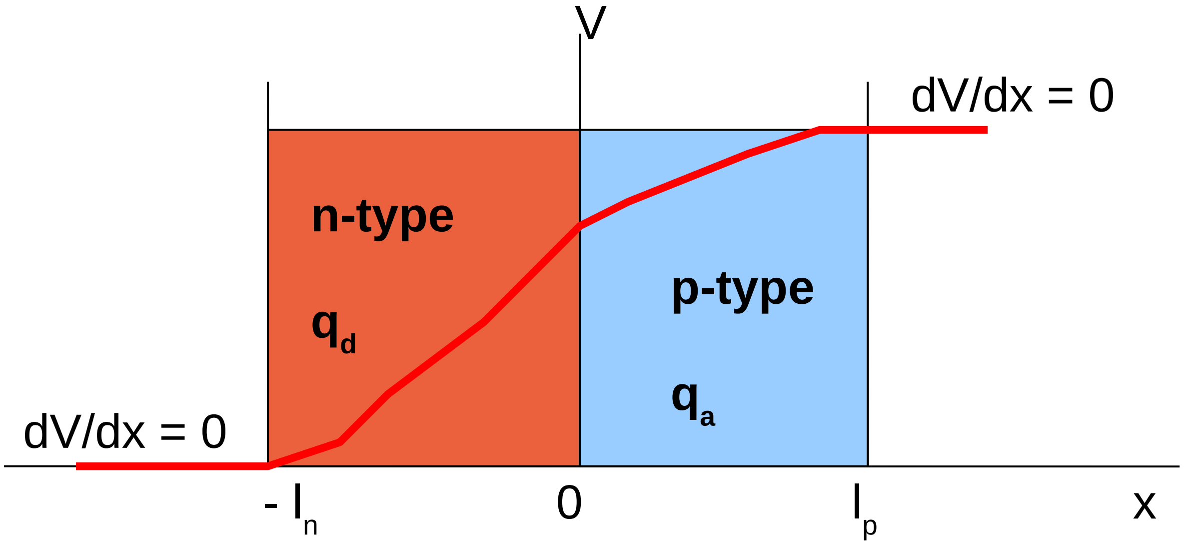
Where ρ is the charge density due to negative acceptor ions (ρ_a) or positive donor ions (ρ_d) in the p- and n- materials respectively. These are fixed charges, not mobile current carriers

Semi-conducting physics

The p-n junction: the depletion layer



A. The depletion layer at a p-n junction



B. Calculation of the width of the layer, See next slide

Semi-conducting physics

The p-n junction: width of the depletion layer

Referring to figure B. (previous slide), the junction is at x=0 and the depletion layer extends to to $-l_n$ and $+l_p$ into the n- and p- type materials respectively, integrating $d^2V/dx^2 = -\rho/\varepsilon\varepsilon_0$ we get: $\varepsilon\varepsilon_0 dV/dx = -\rho_d x + constant$ for the n-type side.

Since $-l_n$ is at the boundary of the depletion layer the electric field (ie $-dV/dx$) will be 0 there (derivative is 0). The constant is therefore $-\rho_d l_n$, so we get: $\varepsilon\varepsilon_0 (dV/dx)_{x=0} = -\rho_d l_n$. For the p-type side: $\varepsilon\varepsilon_0 (dV/dx)_{x=0} = \rho_a l_p$

dV/dx must be the same on either side of the junction (x=0) and so we may equate the two equations: $-\rho_d l_n = +\rho_a l_p$

Thus, on either side the charges are equal and opposite. If N_d and N_a are the respective *numbers* of donor and acceptor atoms per unit volume then $N_d l_n = N_a l_p$ **We therefore see that heavy doping on one side will reduce the width of the depletion layer on that side.**

Semi-conducting physics

The p-n junction: dynamics of the depletion layer

Considering $\varepsilon\varepsilon_0 \, dV/dx = -\rho_d x + constant$ once more and integrating once more between $x = l_n$ and $x = 0$ (remember, we are in the n-type material) we get: $\varepsilon\varepsilon_0(V_0 - V_n) = ½\, \rho_d l_n^2 - ½\, \rho_d l_n^2 = - ½\, \rho_d l_n^2$ and $\varepsilon\varepsilon_0(V_p - V_0) = +½\, \rho_a l_p^2$ for the p-type side.

The total potential across the junction, V, is therefore

$$V = 1/2\varepsilon\varepsilon_0(- ½\, \rho_d l_n^2 + ½\, \rho_a l_p^2)$$

$= -e/2\varepsilon\varepsilon_0(N_d l_n^2 + N_a l_p^2)$, where e is the modulus of the electronic charge. Using $N_d l_n = N_a l_p$ the relationship can also be written as:

$$V = -e/2\varepsilon\varepsilon_0(N_d l_n^2)(1 + N_d/N_a)$$

Semi-conducting physics

The p-n junction: the charge and capacitance of the depletion layer

If we consider the depletion layers to act like a charged capacity then $-eN_dl_n$ will be the charge Q on one side.

It follows that $V = \{ Q^2/2\varepsilon\varepsilon_0 e\}((N_a + N_d)/N_aN_d)$, and so

$$Q = V^{1/2}\{2\varepsilon\varepsilon_0 e(N_aN_d/(N_a + N_d)\}^{1/2,}$$

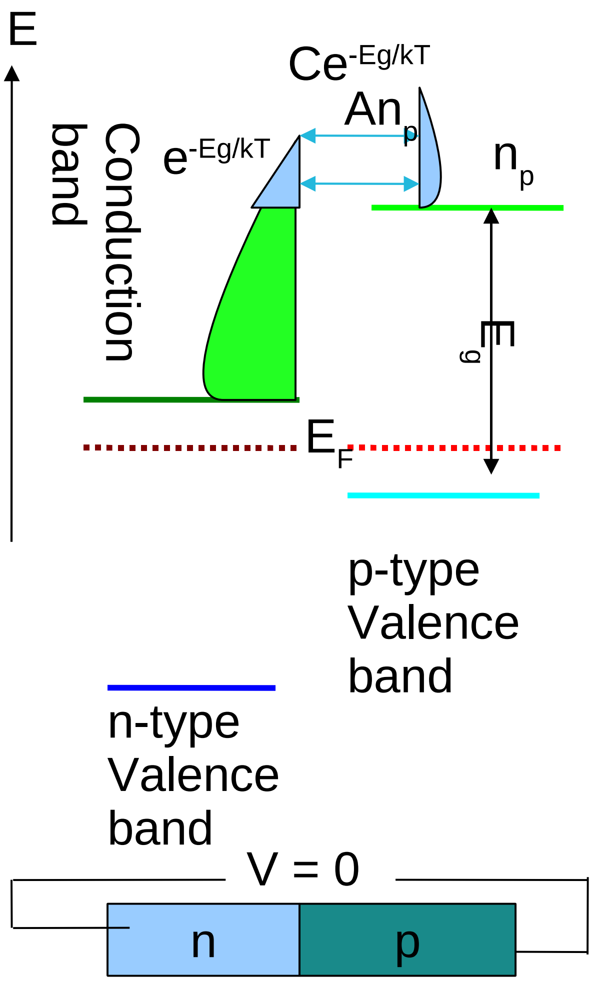
The capacity at the junction, $C = dQ/dV$, is therefore

$$C = ½\, V^{-1/2}\{2\varepsilon\varepsilon_0 e(N_aN_d/(N_a + N_d)\}^{½}$$

If no external potential is applied V is approximately equal to the gap potential. If a potential is applied then V is equal to the gap plus the applied potential. We can therefor saee that the junction can be used as a capacitor which varies as $V^{-1/2}$. This is the basis of the variable capacity diode which is used in frequency locking and frequency modulation circuits.

Semi-conducting physics

The p-n junction: Effects of a potential difference (battery) across the depletion layer: The initial condition with no potential (V = 0)

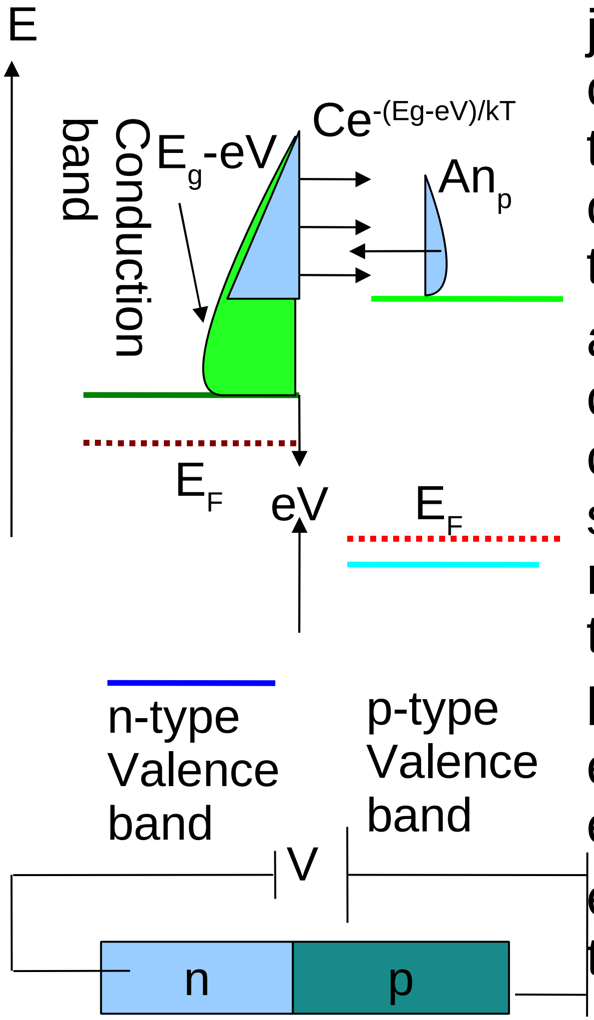


The number of electrons on the p-side is so small that they may all be considered at the bottom of their conduction band (light blue), the number that face them in the n-side will be proportional to $\exp(-E_g/kT)$, assuming Boltzmann statistics where the energy of the of the electrons on the n-side is measured from the bottom of their conduction band and E_g is the width of the energy gap. This represents the junction at equilibrium so that at any instant the number of electrons which diffuse from any level will be proportional to the population at that level:

$C \exp(-E_g/kT) = An_p$ where C and A are constants of proportionality for diffusion from the n- and p- sides respectively

Semi-conducting physics

The p-n junction: Effects of a potential difference (battery) across the depletion layer: positive biasing

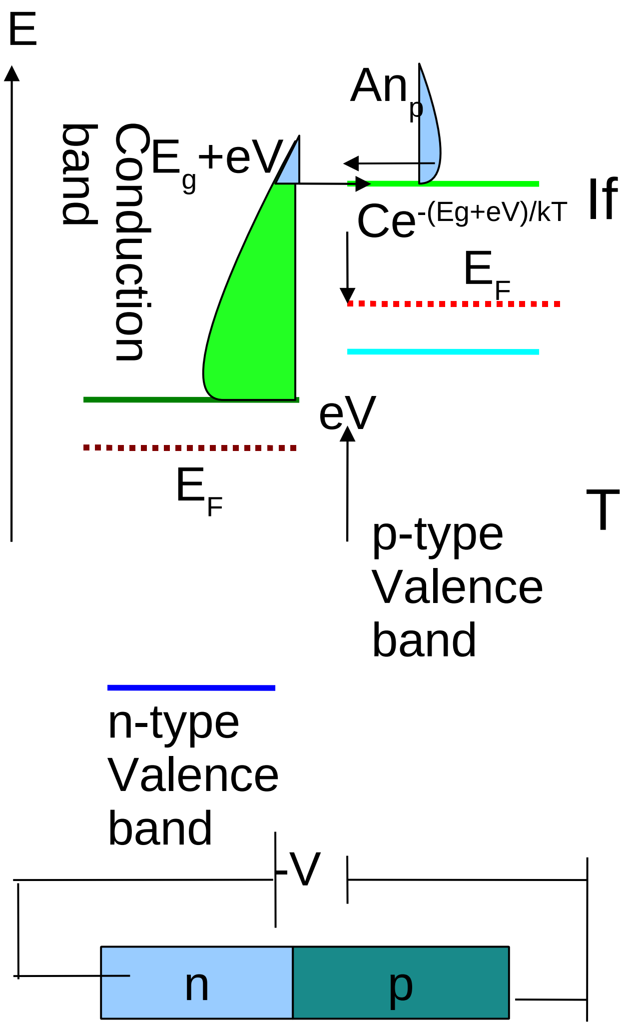


When a battery it produces a potential 'V' across the junction in such a direction that the step between the conduction band is lowered (the conventional positive terminal is connected to the p-side). This is called forward or positive biasing. The bottom of the conduction band on the p-side is now level with an energy E_g-eV on the n-side and so there will be an imbalance in favor of those electrons crossing from n to p but because the junction is part of a closed circuit no pile-up of electrons occurs to increase the step height again because the current can flow. The number of electrons which can flow from n to p is increased to: $C\ exp\{-(E_g-eV)/kT\}$ since more of the n-side conduction band is is now exposed to the p-side. The number of electrons whcih can cross from p to n however cannot exceed An_p. Since this takes into account of *all* the available electrons on the p-side. There will therefore be a net transfer from n to p equal to

$C\ exp\{-(E_g-eV)/kT\} – An_p$ or $An_p[exp\{eV/kT\}$ -1 from previous eq.

Semi-conducting physics

The p-n junction: Effects of a potential difference (battery) across the depletion layer: negative biasing



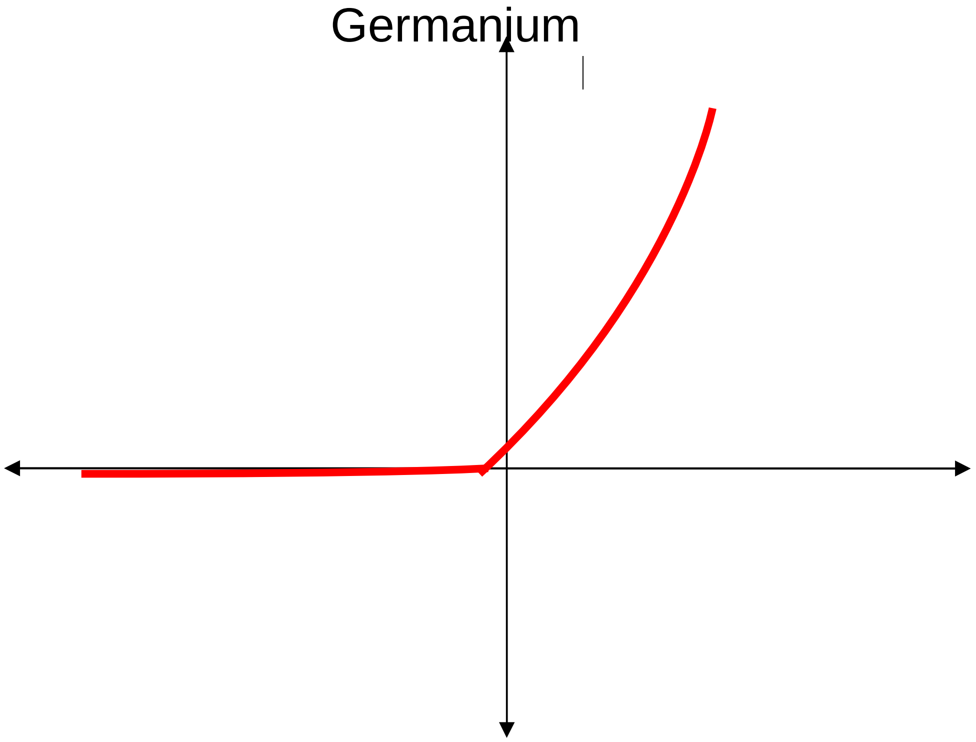
If V was reversed (reverse or negative biasing) the step between the n and p sides would be *increased* to $E + eV$ and the previous equation would become: $An_p[exp\{-eV/kT\} -1$

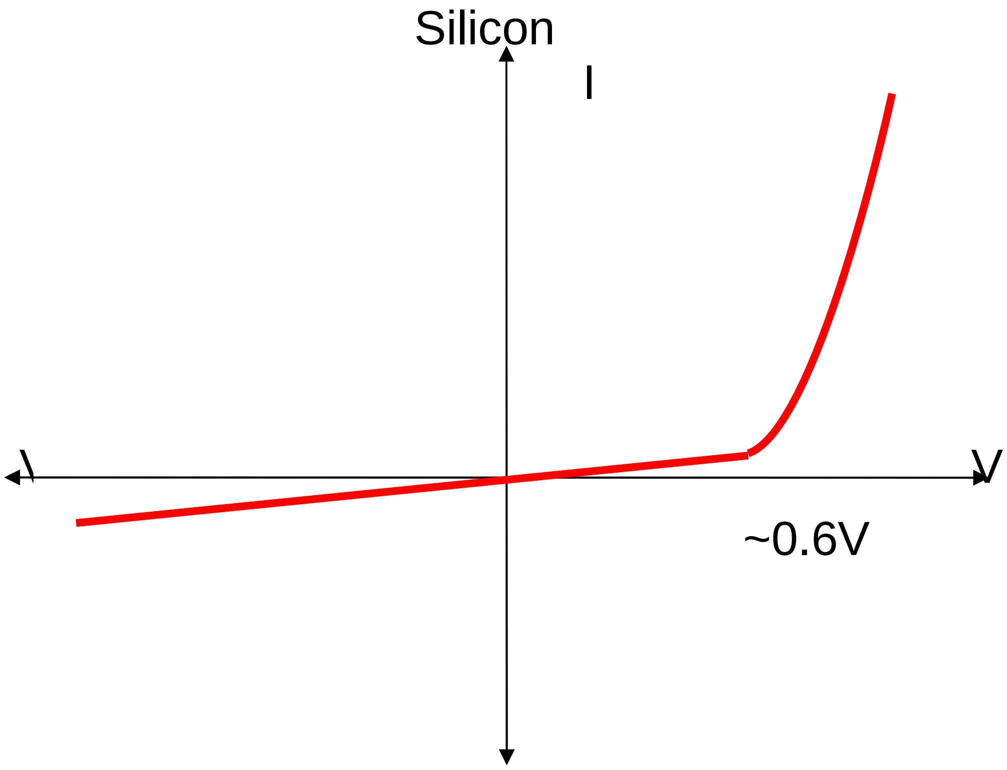
This is negative, ie the concentration of electrons at the junction is *less* than the main body of the p-type material and there is a net transfer of electrons from p to n.

Semi-conducting physics

The p-n junction: current characteristic summary

The p-n junction exerts a remarkable control on the current and this depends on the direction of the applied potential. If the p-side of the junction is made positive the current flows easily and increases rapidly as V is increased. Conversely if V is negative very little current flows and, for large negative values of V, it flattens off to a constant value.


Germanium


Silicon

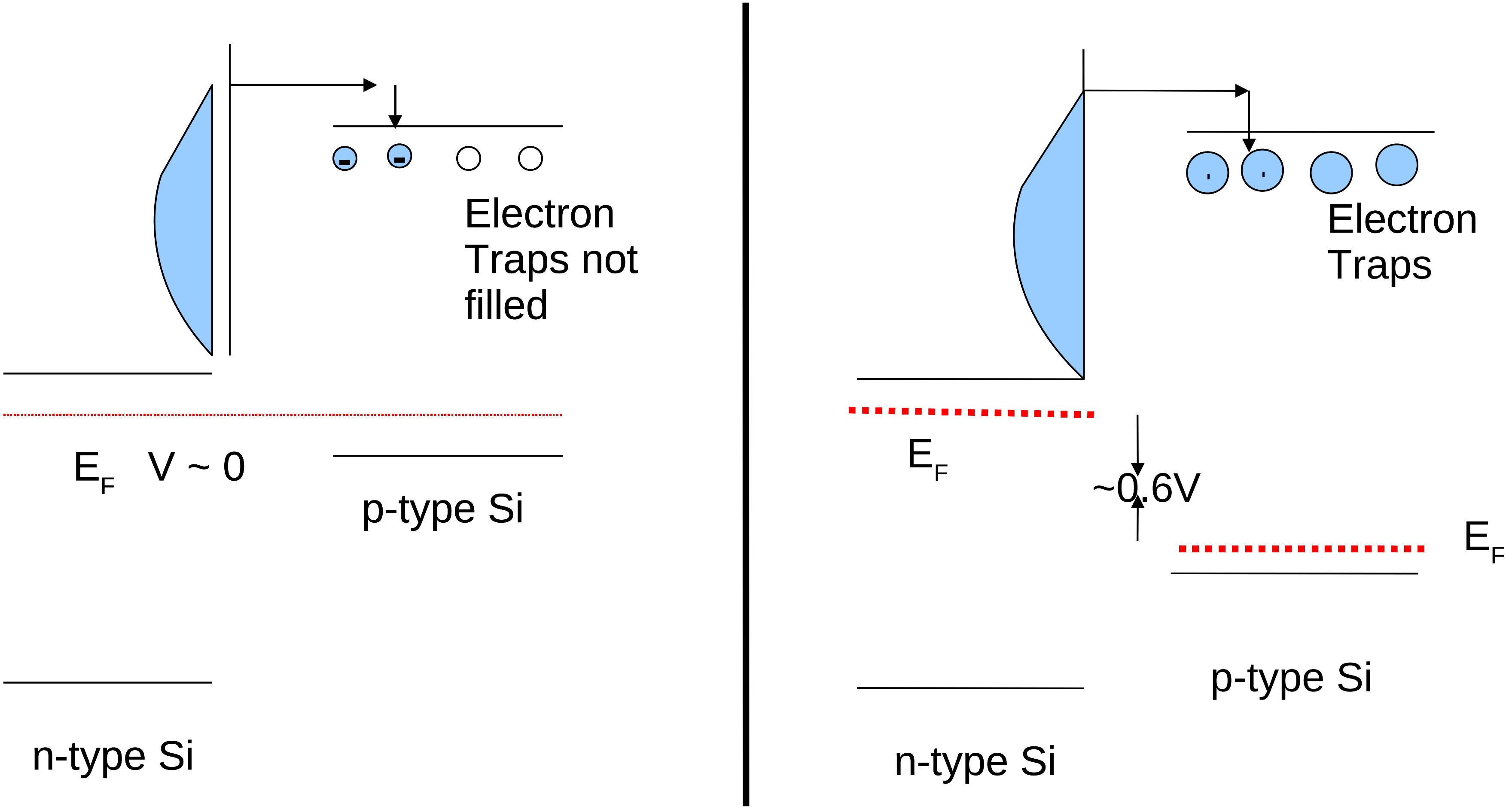
Semi-conducting physics

The p-n junction: Current characteristics for silicon

When a silicon junction is positively biased virtually no current flows until the potential reaches ~ 0.6V and beyond this voltage it increases rapidly. This is probably due to the fact that $N_e N_h$ is low for silicon, the minority carrier concentration is very small. This can provide only an extremely low current close to the origin and even with the exponential rise it takes until 0.6V to build a reasonable value. Another contributory mechanism might be that due to the small minority concentration the electron trps on the p-side of the junction are not full. Hence, immediately electrons cross from the n- to the p-side they are trapped. Only when V is sufficiently large that the step between the bottom of the conduction bands on either side of the junction is reduced and the traps can be filled are there any electorns left over to contribute to the conduction process. **This behaviour at 0.6V is very important in the design of circuits that which use silicon transistors. The base-emitter potential must be set at 0.6V for satisfactory operation**

Semi-conducting physics

The p-n junction: current characteristic for silicon: graphics

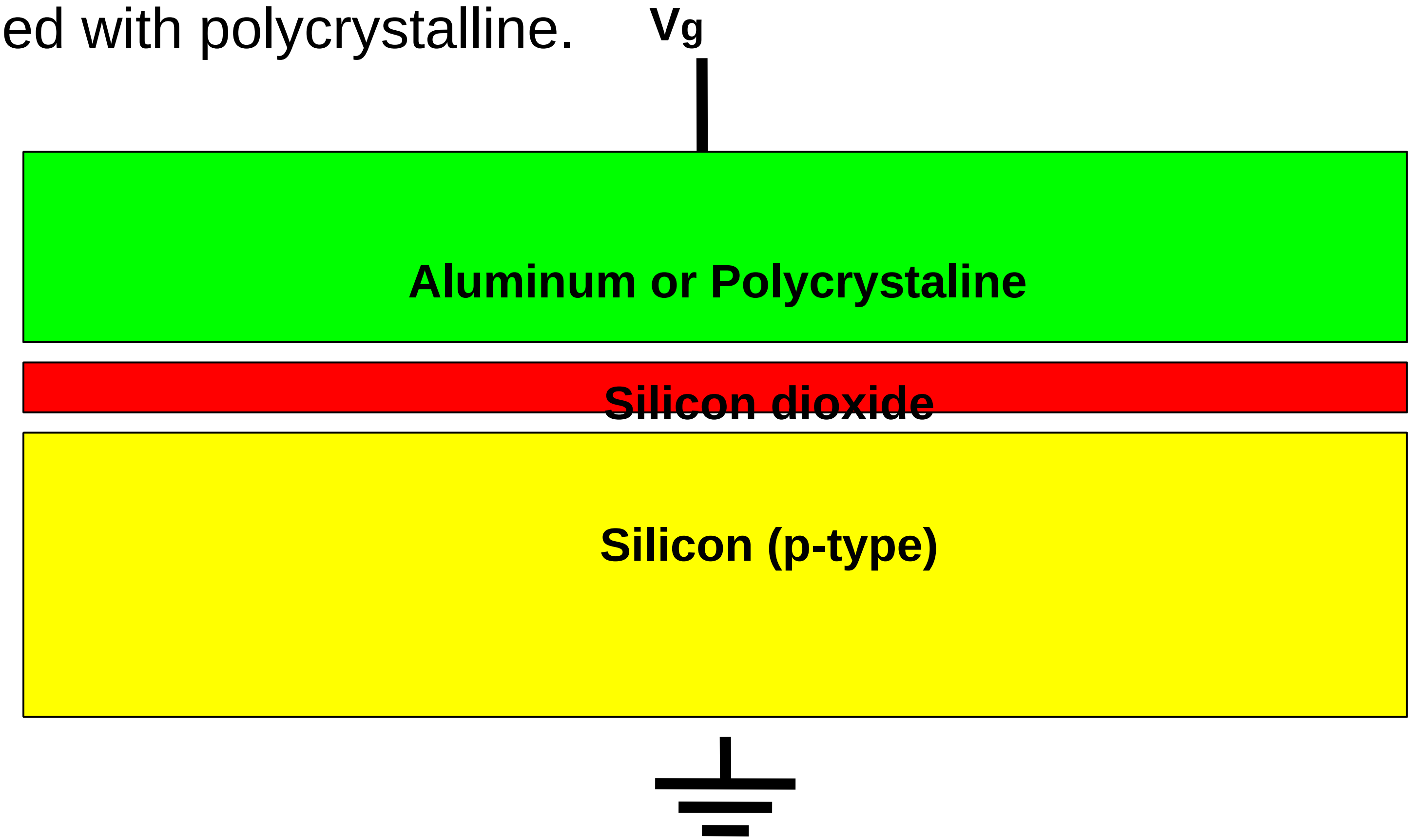


Electron trapping at a silicon p-n junction; Left – for small positive bias carriers fill
Empty traps and no current flows. Right – When the bias is 0.6 V the traps are filled and
The junction conducts.

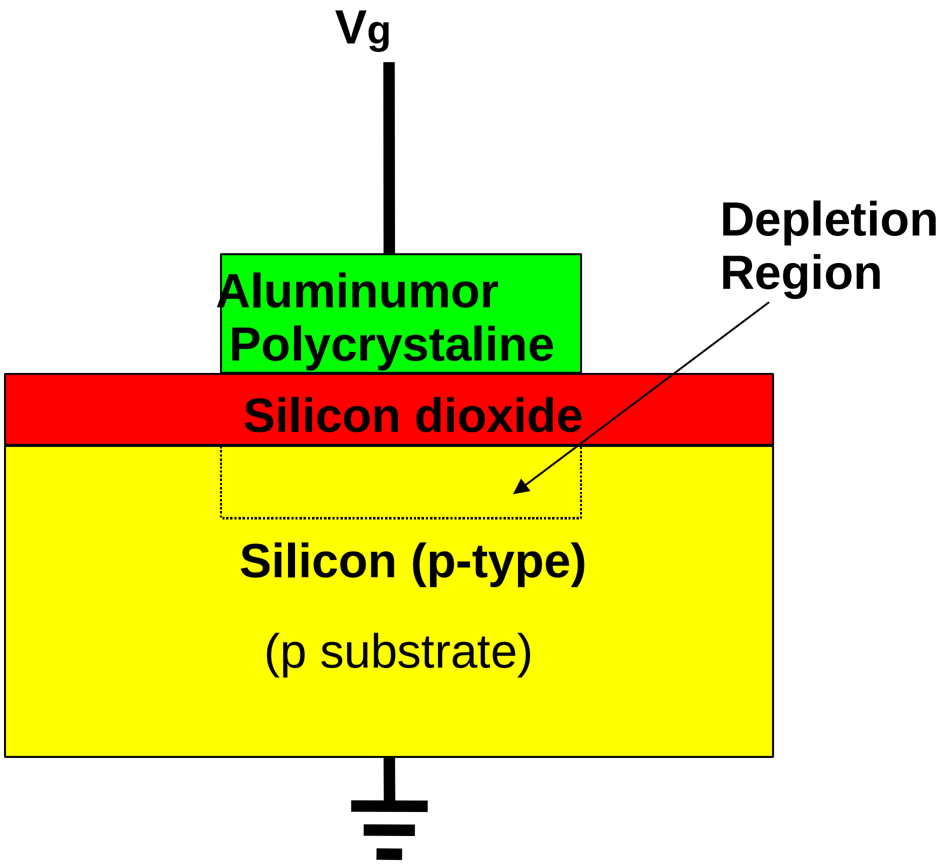
Applying p-n dynamics:

the Metal-Oxide Semiconductor (MOS)

The basics of a MOS capacitor is shown below where the structure comprises an aluminum gate (a metal conductor) over a dielectric insulating material (SiO_2) deposited on a p-type silicon semiconductor. The band gap of the insulator is 8eV while the band gap of silicon is 1.1eV. In recent years the metal gate has been replaced with polycrystalline.



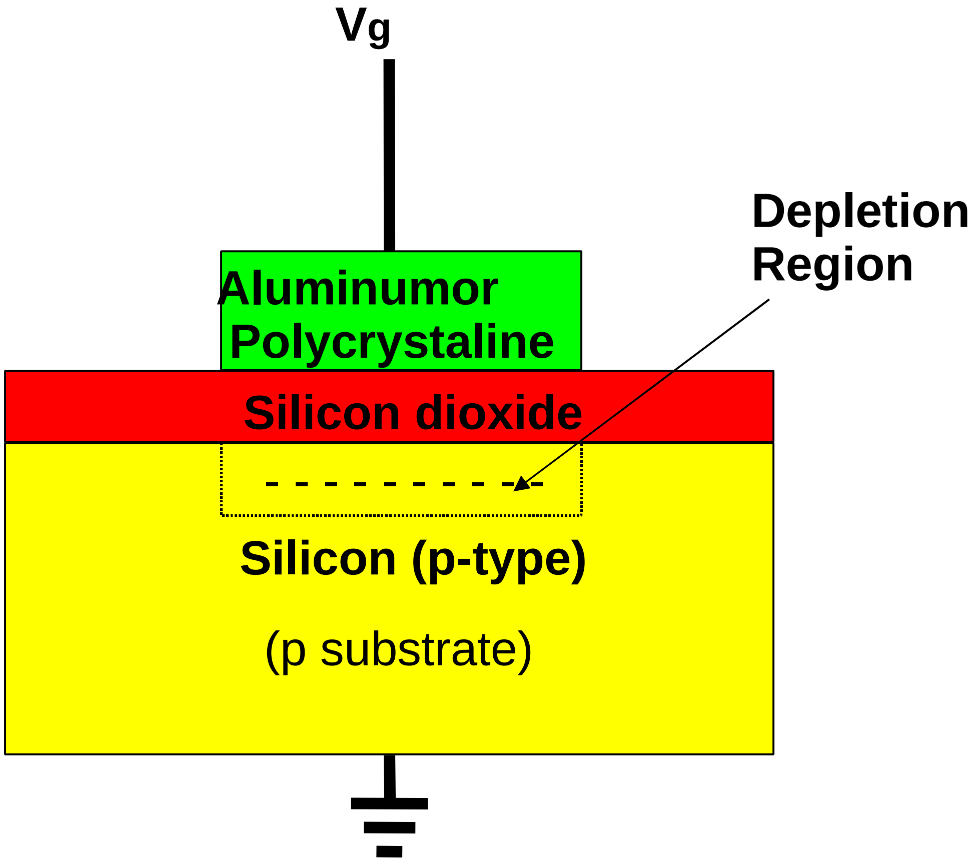
The Metal-Oxide Semiconductor (MOS), single unit or diode



The voltage, V_g, is a sum of the voltage across the insulator (the oxide) V_o, and at the surface of the silicon,&, also called the surface potential: $V_g = V_o +$ &

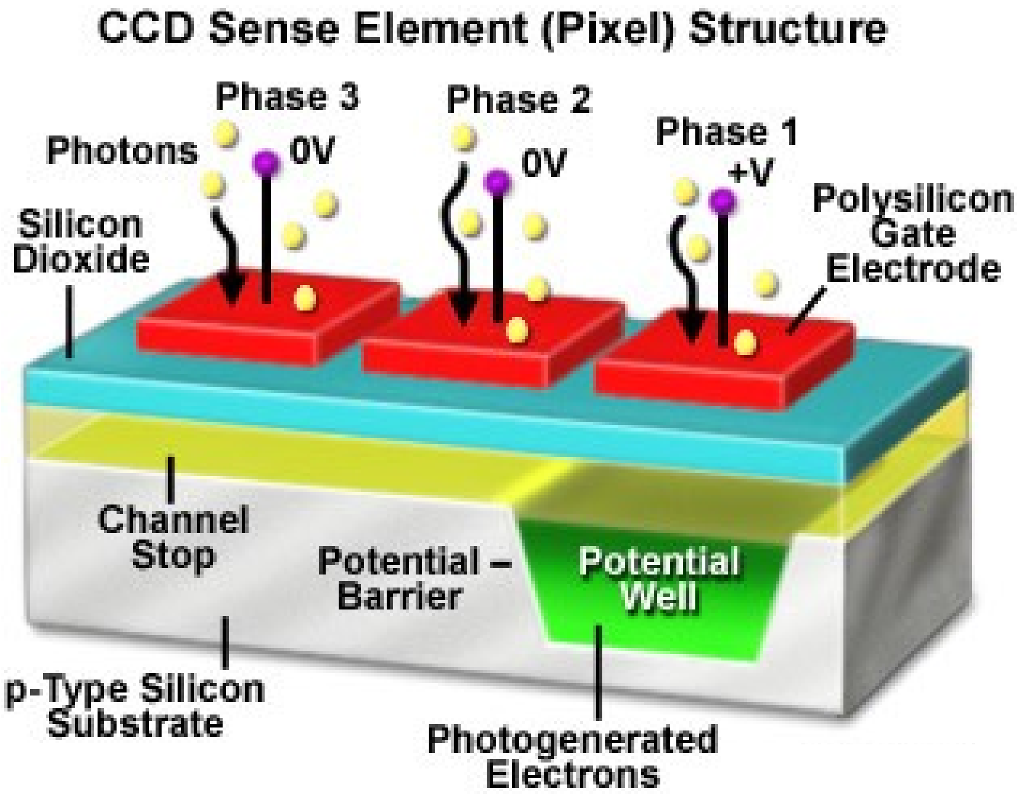
As noted with earlier voltage applied conditions three states are possible with the electrons and holes at the junction interface: a) carrier accumulation b) carrier inversion, and c) carrier depletion. It is carrier depletion that is important with respect to the functioning of the charge coupled device.

The Metal-Oxide Semiconductor (MOS) diode



When a positive bias is applied to the polycrystaline, the majority of holes are repelled – resulting in a depletion region of negatively charged acceptor states under the gate, near the surface of the silicon. This charge would be described by the surface charge $\& = Vg + Q_s/C_0$ where Q_s is the total charge perunit area in the semiconductor surface region (C/cm^2) and C_0 is the SiO2 Capacitance (F/cm^2). The oxide capacitance Co is given by $C_0 = K_0 \ e_0/x_0$ where K is the oxide dielectric constant (3.9 for silicon dioxide), e is the free space permittivity (F/m) and x is the oxide thickness

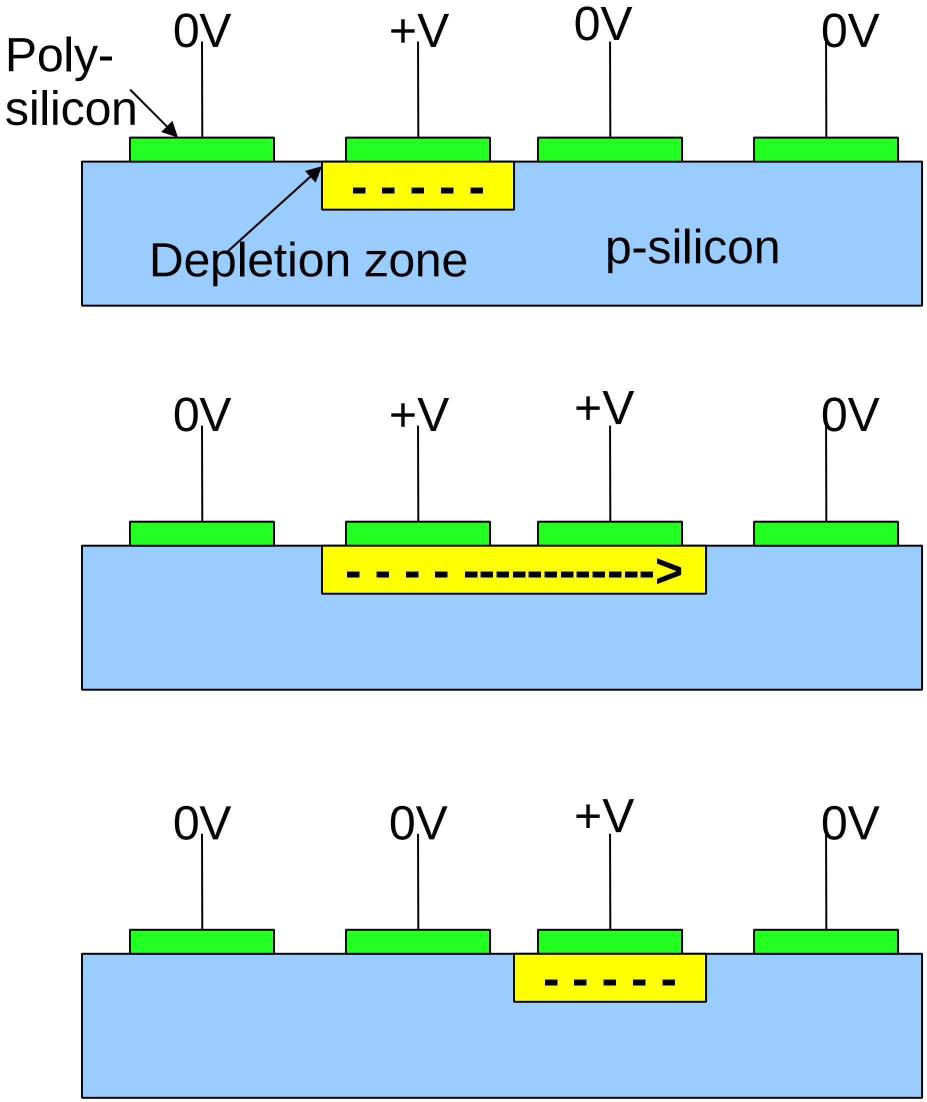
Applying the MOS diode basics to the charge coupled device



A three phase CCD pixel. The potential well
Is another term for the depletion zone. The
Channel stop is typically an n-type silicon
Designed to prevent photo generated electrons
From 'leaking' from the depletion zone

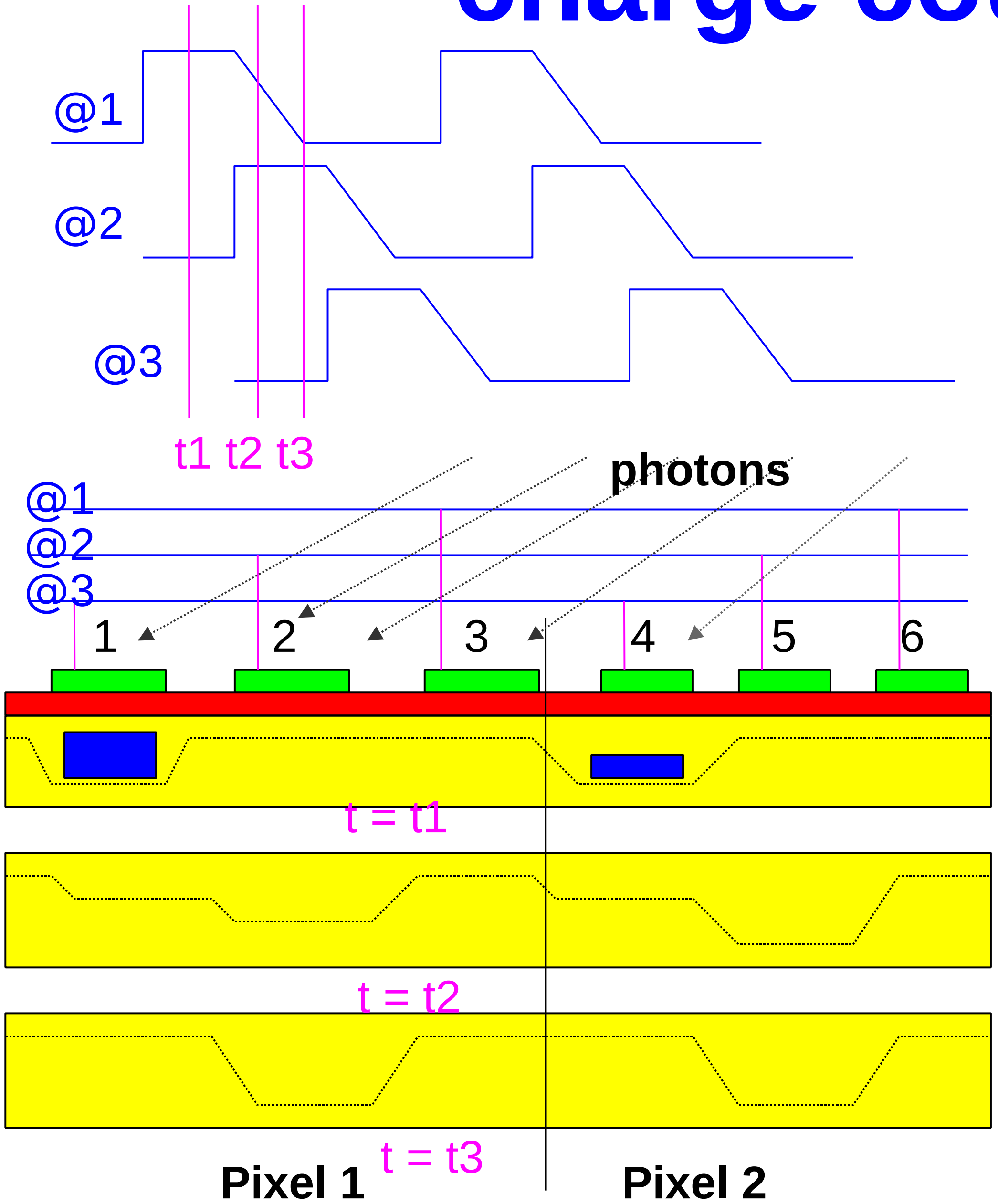
The CCD is a series of MOS units designed to accomplish the task of collecting and storing electrons generated by photons (the MOS device does this on its own) and transferring those electrons to a point for measurement The MOS array, or CCD, performs this action via a phased applied voltage. Charge coupling refers to the method by which the photo-electrons are transferred by each MOS unit and applied positive voltage.

Photo-electron signal transfer by charge coupling



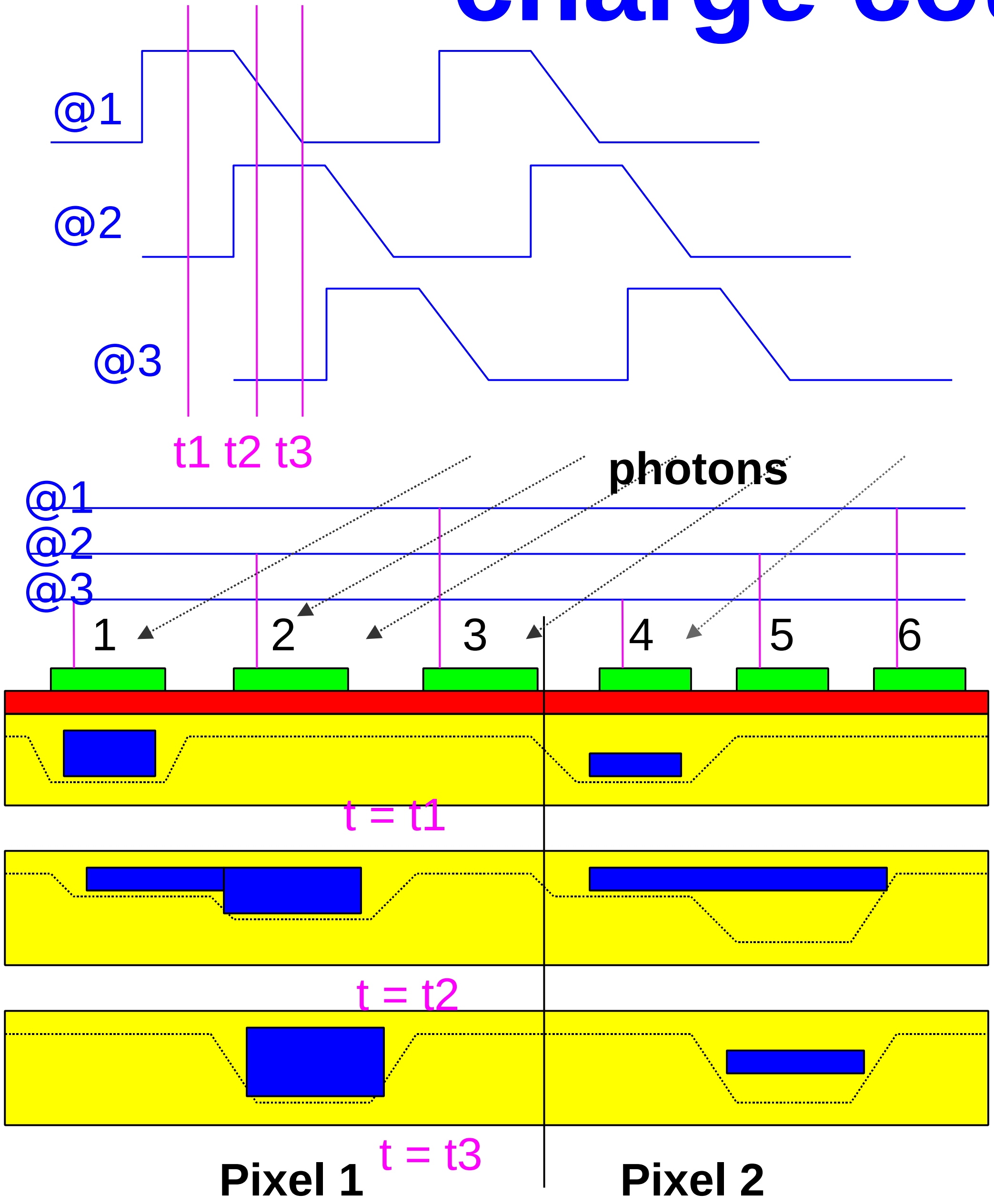
1. The charge is localised under the gate with the highest applied potentials because the positive bias (Vg) causes the underlying silicon to be in depletion state ie holes are created and electrons fill the depletion zone.
2. As the voltage of the adjacent gate is positively biased another depletion zone is formed and the electrons 'spill' into the adjacent potential well.
3. With a series of alternating voltage pulses, the electrons can be transferred down the array to a final output measurement device

Three phase signal transfer by charge coupling - 1



- Three phase drive pulses(@) can be applied to drive the charge from one MOS unit to the other, in this case three MOS units make a pixel.
- If the positive voltage applied to @1 is higher than that applied to @2 and @3, surface potential wells are produced under the @1 gate.
- Charge packets introduced either optically or electrically are accumulated in these depletion wells at t = t1. These charge packets may be of different signal strengths as noted under gate 1&4 (blue area 'electrons')

Three phase signal transfer by charge coupling - 2

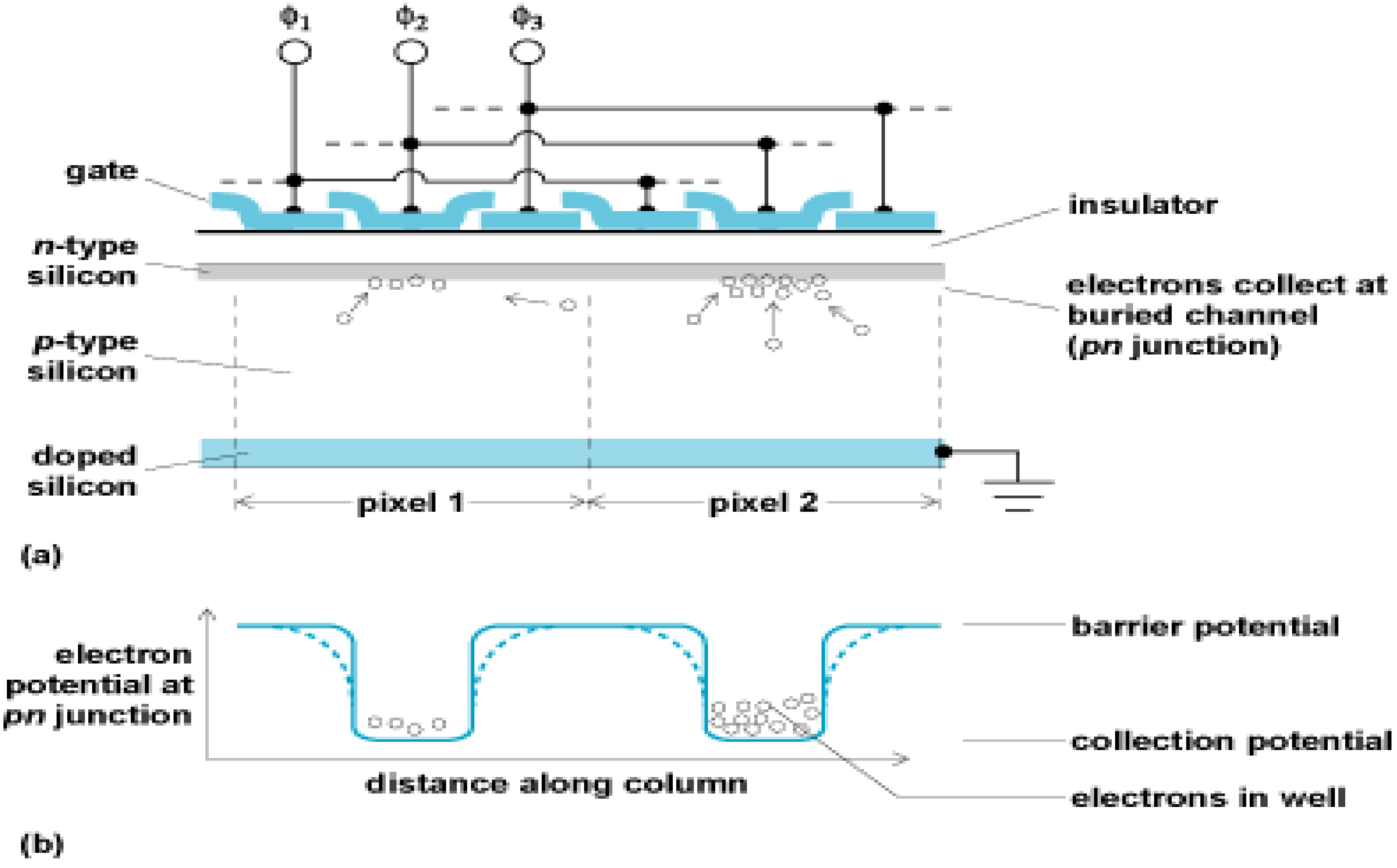


- Moving the charges to right requires a positive voltage applied to @2 to ensure that the potential wells under gates @1 and @2 are the same depth.
- The charge packets are allowed to spread to the right as noted in t = t2.
- Immediately after the the pulse to @2 the voltage at @1 decays so that the potential well under gates 1 and 4 slowly rise.
- The charge packets now spill over to potential wells in gates 2 and 5 at t = t3
- At each full cycle of clock voltages the charge packets advance one pixel R

Surface channel vs. buried channel CCDs

- CCDs described so far store transfer their charges in potential wells situated at the silicon *surface* underneath the silicon dioxide under the gates. They are known as surface-channel CCDs (SCCDs).
    - These surface states can be adversely influenced by such things as transfer efficiency and noise levels – particularly if the signal strength is low.
- The buried-channel CCD overcomes the worst of these problems. It is created by coating a diffused n-type layer on a p-type substrate.
    - If a large positive voltage is applied to the channel at a gate, then a depletion layer is formed under the MOS gates. (see next slide, positive bias under phi2)
    - The potential well formed in the n-type buried channel will then store the signal electrons, which can then be transferred by the same clock pulses in SCCDs
    - BCCDs transfer efficiencies can be upto 99.99%

Surface channel vs. buried channel CCDs

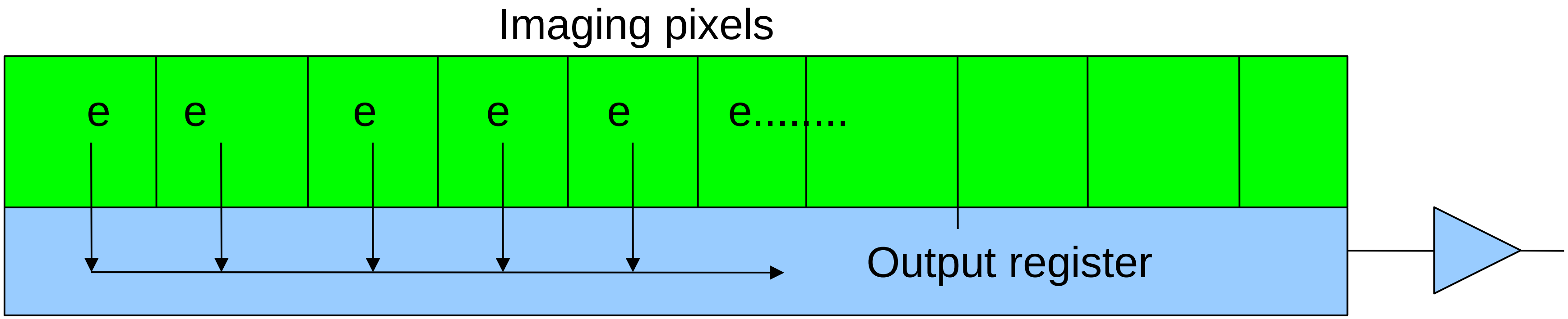


CCD Imaging Architectures

The single array CCD

The single array CCD represents the simplest and earliest form of digital imager and has been used in satellite remote sensing since the early 70's. Leica introduced this type sensor in its photogrammetric cameras in 2000. Generally not used in professional and amateur imaging devices but exclusively used in scanning systems.

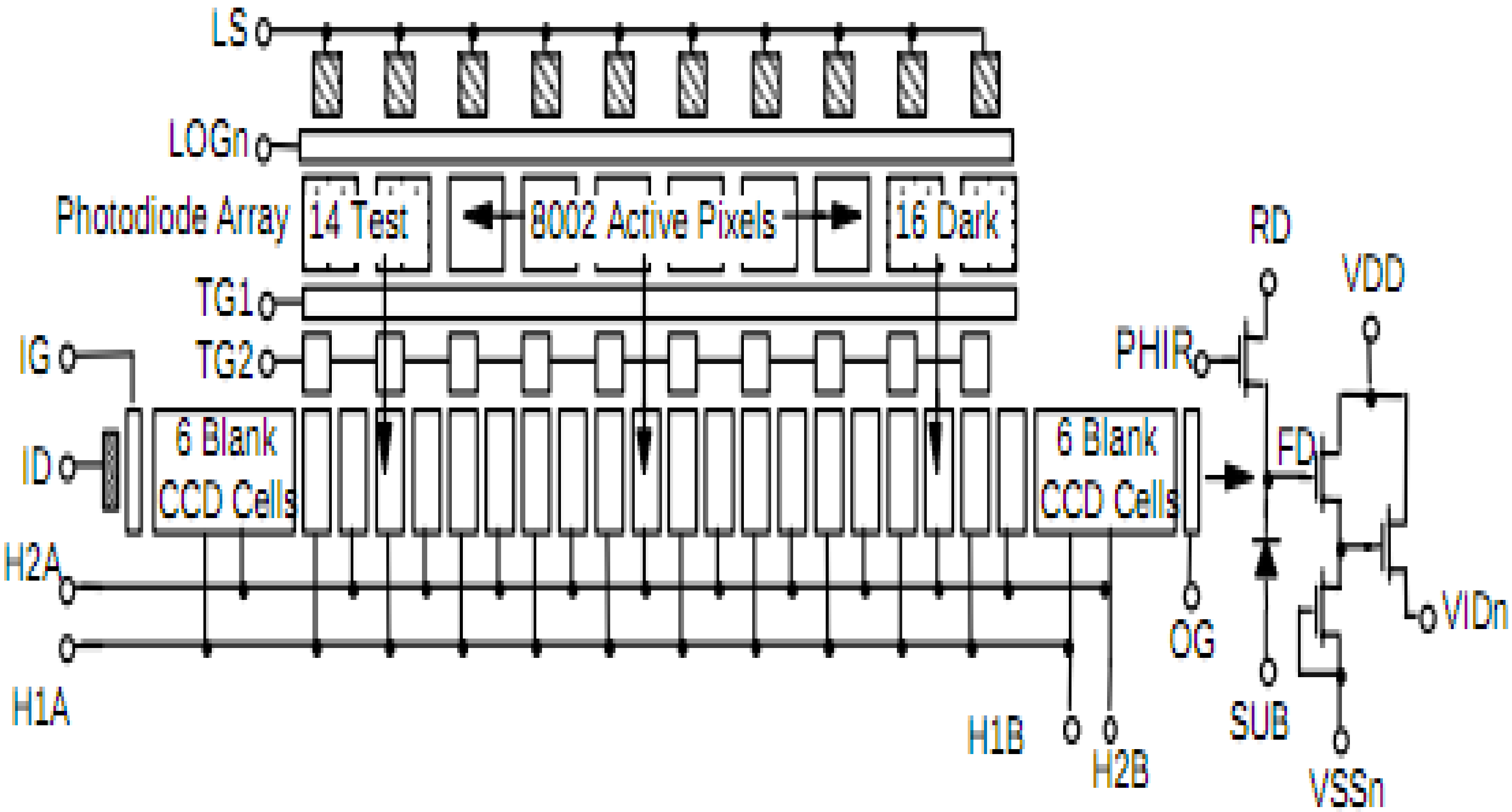
The basic function of the linear CCD is noted below



The linear array sweeps forward to scan the object in a regular pattern that is read out strip by strip via the output register in to storage or direct transmission.

CCD Imaging Architectures

Single line CCDs: the Kodak KLI-8023



CCD Imaging Architectures

Single line CCDs: the Kodak KLI-8023

Functional description: from SPECIFICATION SUPPLEMENT Revision 4.0 MTD/PS-0219

IMAGE ACQUISITION

During the integration period, an image is obtained by gathering electrons generated by photons incident upon the photodiodes. The charge collected in the photodiode array is a linear function of the local exposure. The charge is stored in the photodiode itself and is isolated from the CCD shift registers during the integration period by the transfer gates TG1 and TG2, which are held at barrier potentials. At the end of the integration period, the CCD register clocking is stopped with the H1 and H2 gates being held in a 'high' and 'low' state respectively. Next, the TG gates are turned 'on' causing the charge to drain from the photodiode into the TG1 storage region. As TG1 is turned back 'off' charge is transferred through TG2 and into the PHI1 storage region. The TG2 gate is then turned 'off', isolating the shift registers from the accumulation region once again. Complementary clocking of the H1 and H2 phases now resumes for readout of the current line of data while the next line of data is integrated.

CCD Imaging Architectures

Single line CCDs: the Kodak KLI-8023

Functional description: from SPECIFICATION SUPPLEMENT
Revision 4.0 MTD/PS-0219

CHARGE TRANSPORT

Readout of the signal charge is accomplished by twophase, complementary clocking of the H1 and H2 gates. The register architecture has been designed for high speed clocking with minimal transport and output signal degradation, while still maintaining low (6.25Vp-p min) clock swings for reduced power dissipation, lower clock noise and simpler driver design. The data in all registers is clocked simultaneously toward the output structures. The signal is then transferred to the output structures in a parallel format at the falling edge of the H2 clocks. Resettable floating diffusions are used for the charge-to-voltage conversion while source followers provide buffering to external connections. The potential change on the floating diffusion is dependent on the amount of signal charge and is given by dVFD = dQ/CFD. Prior to each pixel output, the floating diffusion is returned to the RD level by the reset clock, PHIR.

CCD Imaging Architectures

The area array CCD

Three types of designs are encompassed by area array CCDs; all are matrix designs but differ in the manner the electron signal is collected from the pixel and transferred to the amplification, quantising and storage units.

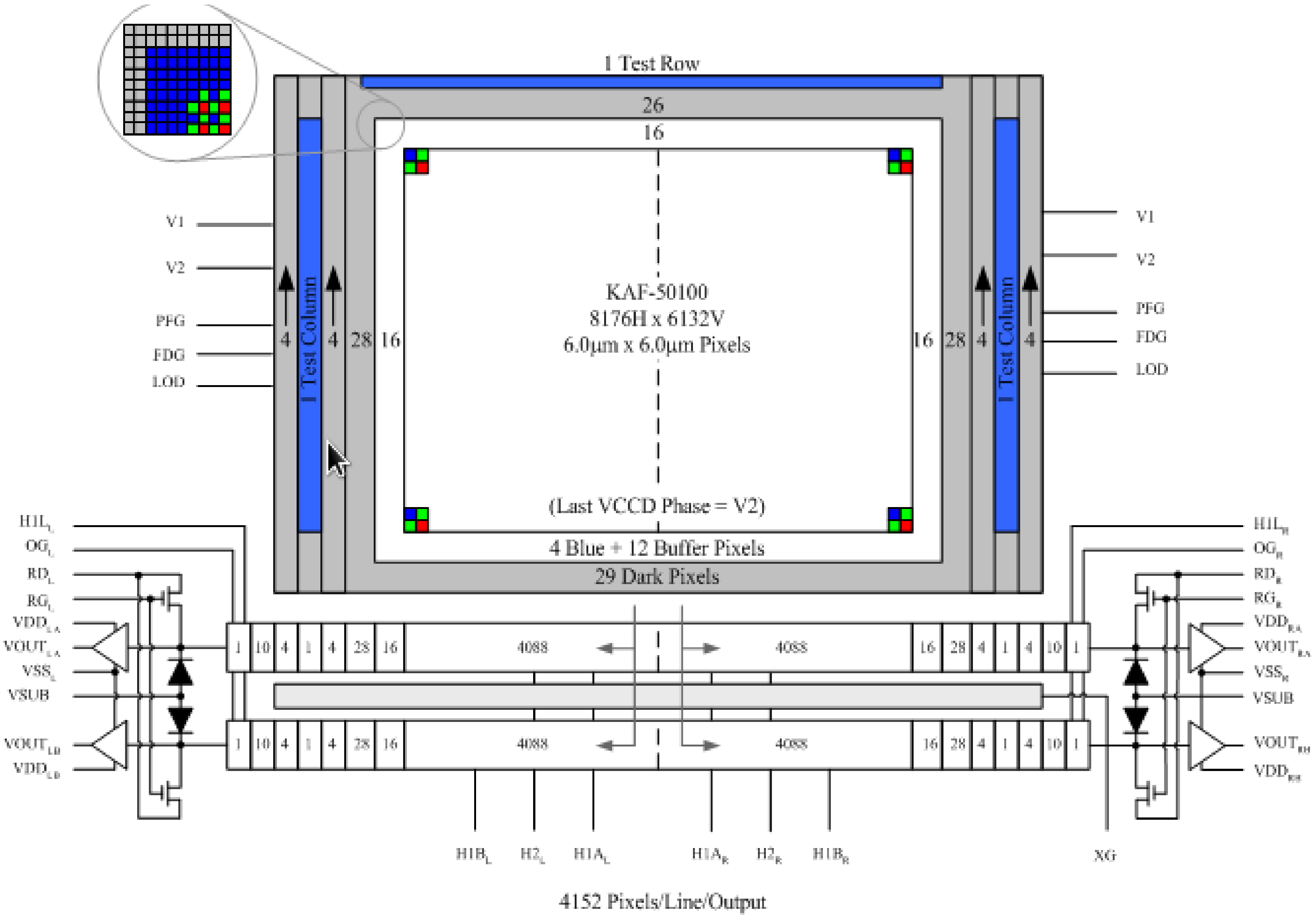
The three types are:

- Interline transfer arrays
- Field-frame transfer arrays
- Full frame transfer arrays

All three have specific uses and may be favoured for one application over another. For digital cameras, the full frame transfer array is currently being favoured as the state-of-the-art choice. We shall focus on this type.

CCD Imaging Architectures

Area array CCDs: the Kodak KAF-50100



CCD Imaging Architectures

Area array CCDs: the Kodak KAF-50100

DEVICE PERFORMANCE SPECIFICATION revision 4.1 MTD/PS-1071

IMAGE ACQUISITION

An electronic representation of an image is formed when incident photons falling on the sensor plane create electron-hole pairs (charge) within the device. These photon-induced electrons are collected locally by the formation of potential wells at each pixel site. The number of electrons collected is linearly dependent on light level and exposure time and non-linearly dependent on wavelength. When the pixel's capacity is reached, excess electrons are discharged into the lateral overflow drain (LOD) to prevent crosstalk or ‘blooming’. During the integration period, the V1 and V2 register clocks are held at a constant (low) level.

CCD Imaging Architectures

Area array CCDs: the Kodak KAF-50100

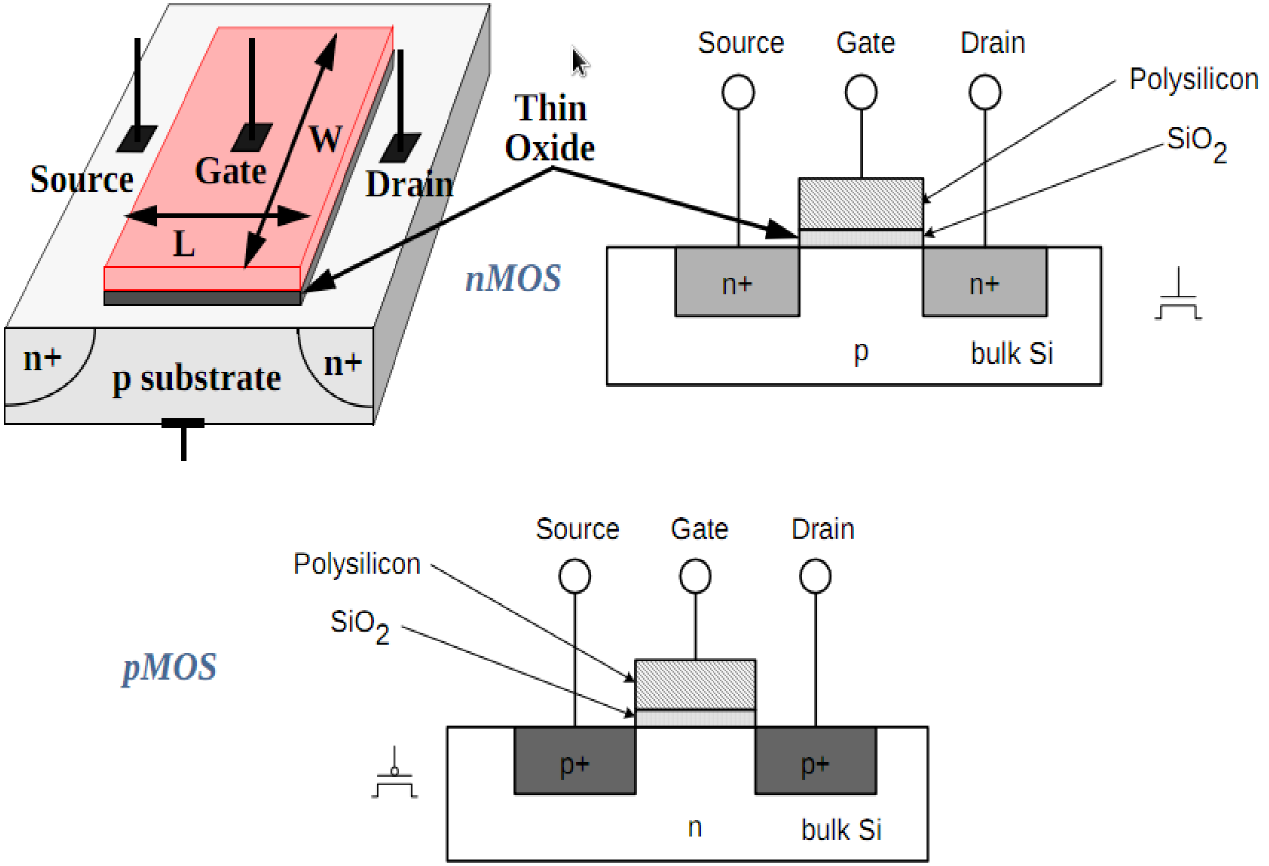
DEVICE PERFORMANCE SPECIFICATION revision 4.1 MTD/PS-1071

CHARGE TRANSPORT

The integrated charge from each pixel in the Vertical CCD (VCCD) is transported to the output using a two-step process. Each remaining line (row) of charge is first transported from the VCCD to a dual parallel split horizontal register (HCCD) using the V1 and V2 register clocks. The transfer to the HCCD occurs on the falling edge of V2 while H1A is held high. This line of charge may be readout immediately (dual split) or may be passed through a transfer gate (XG) into a second (B) HCCD register while the next line loads into the first (A) HCCD register (dual parallel split). Readout of each line in the HCCD is always split at the middle and, thus, either two or four outputs are used. Left (or right) outputs carry image content from pixels in the left (or right) columns of the VCCD. A separate connection to the last H1 phase (H1L) is provided to improve the transfer speed of charge to the output amplifier. On each falling edge of H1L, a new charge packet is sensed by the output amplifier. Left and right HCCDs are electrically isolated from each other except for the common transfer gate (XG).

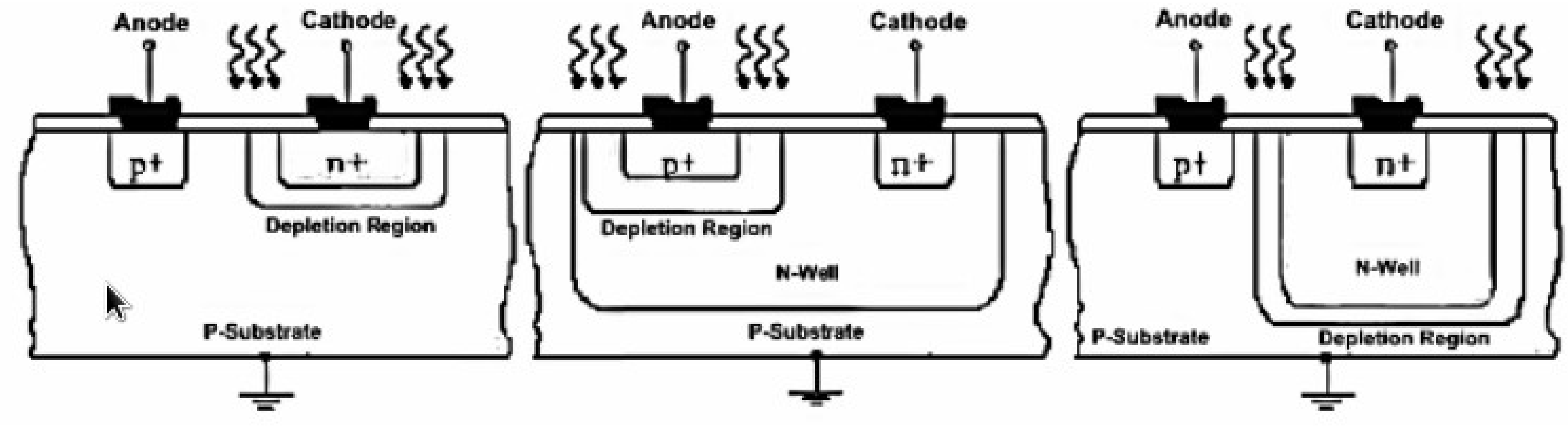
The *Complementary* Metal-Oxide Semiconductor (CMOS)

The complementary metal oxide semiconductor utlizes both n-type and p-type doped silicon in manipulating the charge built by the photoelectric effect. The main difference between the CCD and the CMOS photodiodes is that in the CCD the charge is transported to the processing mechanisms of the sensor via sequential voltages whereas in a CMOS the charge is channeled (L) by a source and drain potential.



The CMOS photodiode

Three basic approaches are used to enable photo charge creation (integration time), each based on whether the potential well needs to be shallow or deep. This will discussed further in relation to the Foveon sensor.

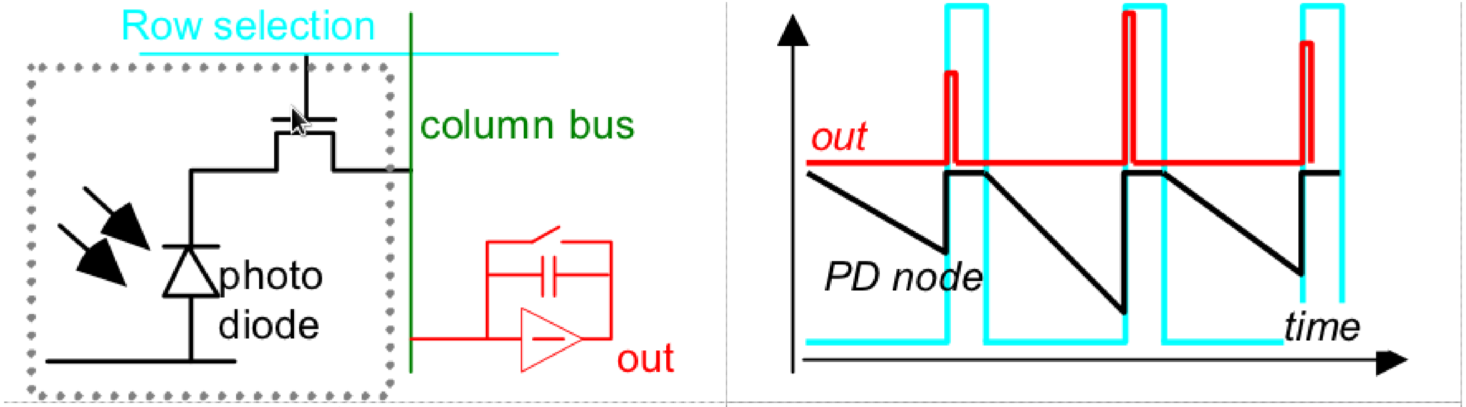


n+ -p(epi)   p+ -nwell   nwell -p(epi)

The CMOS photodiode: Passive and Active pixel structures

The main difference between the passive and active approaches is *where* the processing of the charge signal takes place. The passive pixel structure consists of the photodiode and a reset transistor connected to a vertical column bus. Signal processing (amplification, ADC, etc..) is performed off pixel.

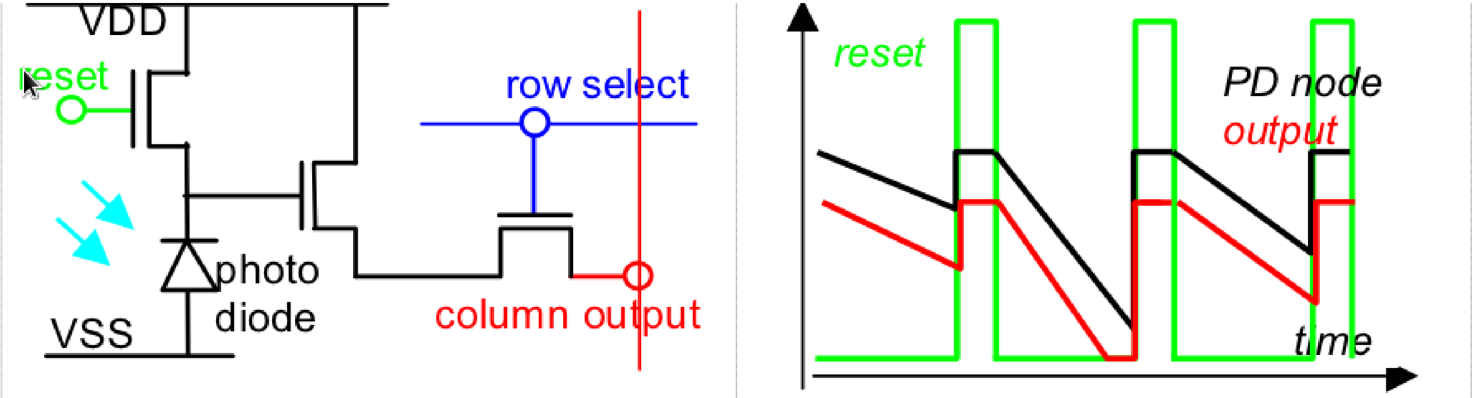
The Passive Pixel Circuit



Pixel Schematic

Pixel voltages versus time

With the Active Pixel Sensor (APS), the amplifier is integrated with the pixel circuit and often more of the processing components are also on the pixel. This basic design is designed as a 3T photodiode



Schematic

Pixel voltages versus time

The Active Pixel Circuit

The CMOS photodiode: An integrated APS

The diagram on the right (from Olympus) characterizes the 3T or 4T photodiode. It is important to note that a significant portion of the pixel surface is not photosensitive (occupied by processing transitors). The effect of this is to reduce the sensitivity of the CMOS photodiode. A microlens is typically added to the surface to focus photons onto the photodiode thus increasing the pixel's light capture capacity.

Anatomy of the Active Pixel Sensor Photodiode

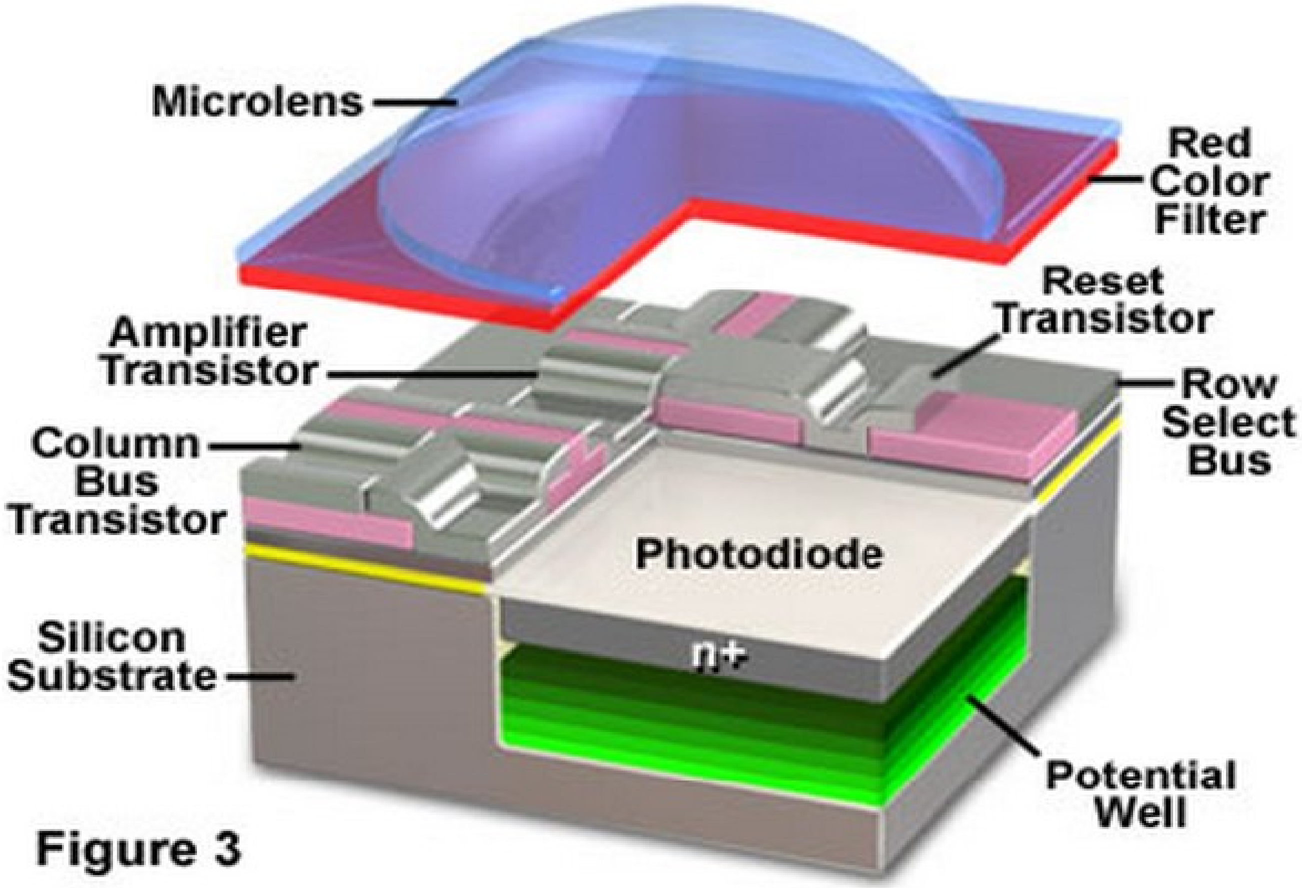
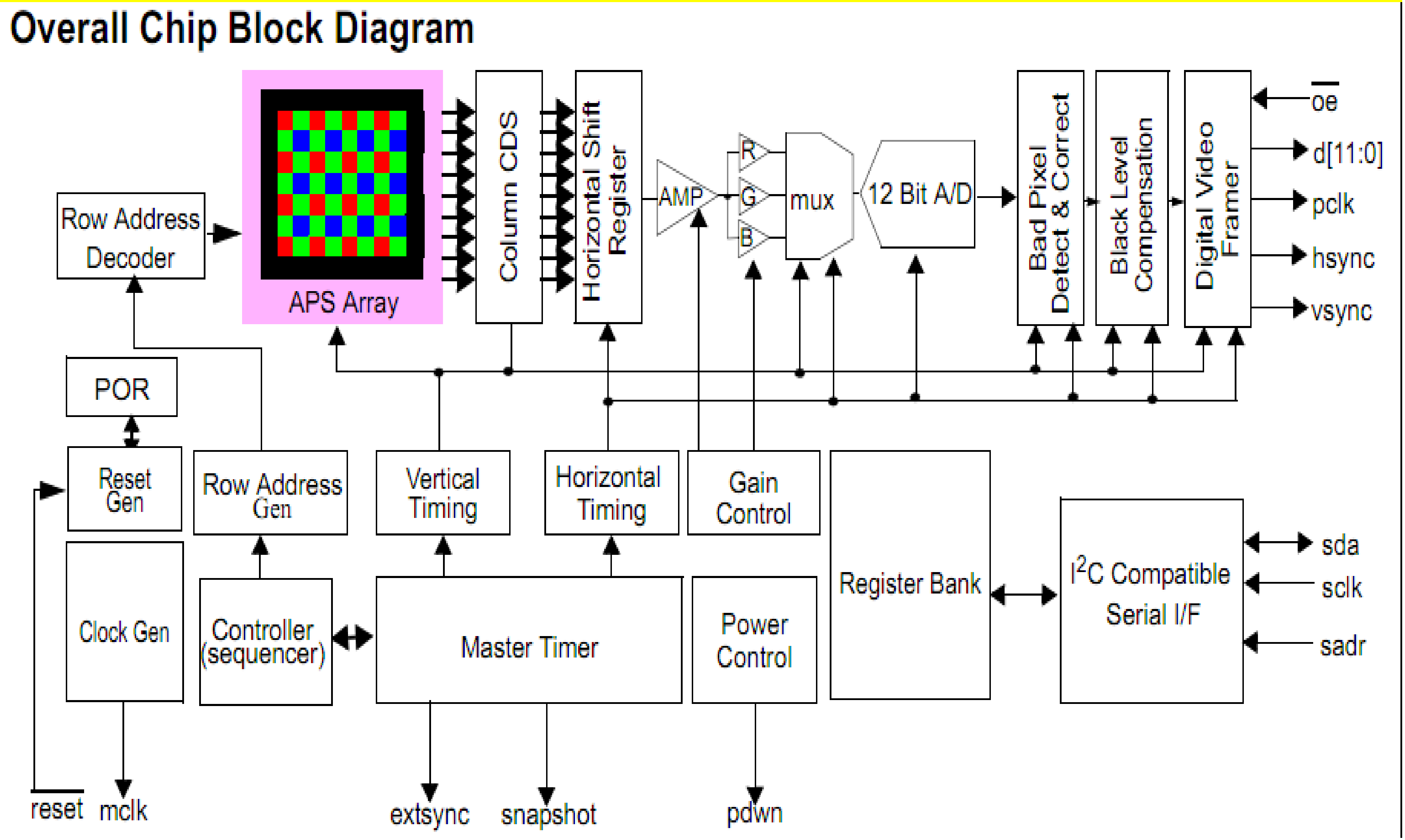


Figure 3

The CMOS Imaging Architectures

An example: Kodak's KAC-9628 Color High Dynamic Range CMOS Image Sensor VGA 30 FPS

KAC-9628



The CMOS Imaging Architectures

Kodak's KAC-9628 Color High Dynamic Range CMOS Image Sensor VGA 30 FPS: Process description

From KODAK KAC-9628CMOS IMAGE SENSOR, Rev 2.0 2007

The KAC-9628 contains a CMOS active pixel array consisting of 488 rows by 648 columns. This active region is surrounded by 8 columns and 8 rows of optically shielded (black) pixels. At the beginning of a given integration time the on-board timing and control circuit will reset every pixel in the array one row at a time. At the end of the integration time, the timing and control circuit will address each row and simultaneously transfer the integrated value of the pixel to a correlated double sampling circuit and then to a shift register. Once the correlated double sampled data has been loaded into the shift register, the timing and control circuit will shift them out one pixel at a time starting with column “a”. The pixel data is then fed into an analog video amplifier, where a user programmed gain is applied, then to the color amplifiers (red, green, blue), where each color gain can be individually adjusted. After gain and color gain adjustment the analog value of each pixel is converted to 12 bit digital data.

Analog Signals Conditioning & Conversion to Digital
The digital pixel data is further processed to:
- remove defects due to bad pixels,
- compensate black level, before being framed and presented on the digital output port

The programming, control and status monitoring of the KAC-9628 is achieved through a two wire I2C compatible serial bus. Additional control and status pins: snapshot and external eventsynchronization are provided allowing the latency of the serial control port to be bypassed during single frame capture.

Photodiode performance factors

- Charge generation
  - Quantum Efficiency (QE), Dark Current
- Charge collection
  - full well capacity, pixels size, pixel uniformity, defects, diffusion (Modulation Transfer Function, MTF)
- Charge transfer
  - Charge transfer efficiency (CTE), defects
- Charge detection
  - Readout Noise (RON), linearity

Photodiode performance factors

Quantum efficiency (QE)

Quantum efficiency is defined simply as:

- **The number of electrons produced per incoming photons or**
  - $QE = N_e/N_{photons}$

The relationship is dependent on:

- The wavelength of the photon
- The material characteristics (thickness, reflection, etc.)
- p-n electric fields

Photodiode performance factors

Quantum efficiency - wavelength

- The electro-magnetic energy required to create the photoelectric effect in silicon is 1.12eV.

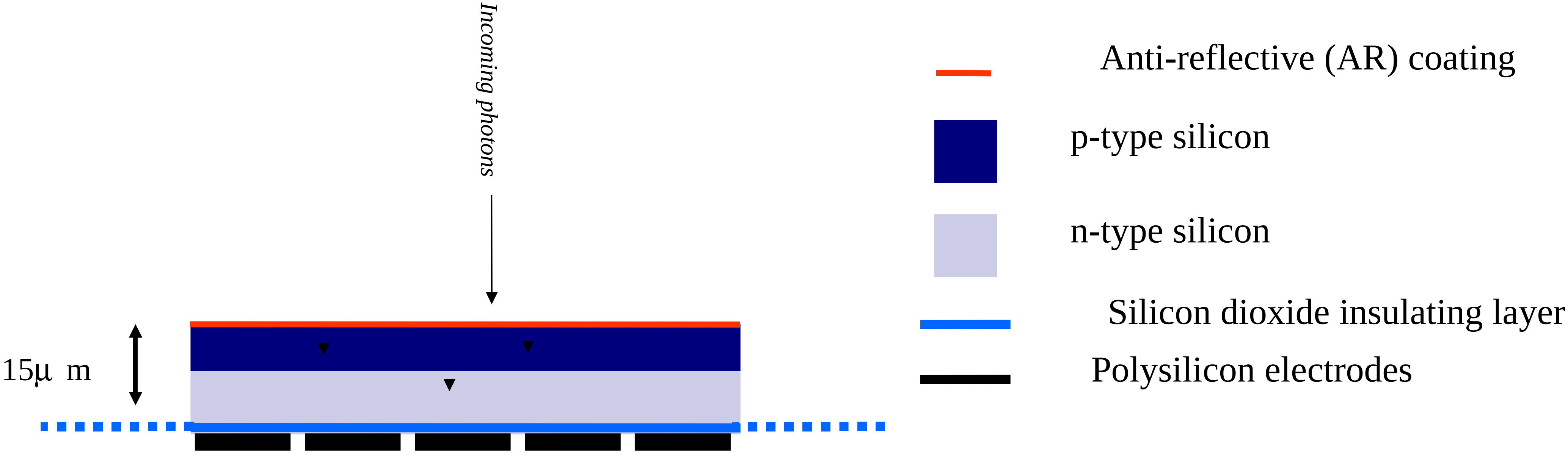
Using Planck's Law: $E = h\nu$, where h is Planck's constant and v is the frequency of light, or 1/λ, then we can equate the energy value with a wavelength. This wavelength is 1100 nanometers, typically called near infrared sensitivity. This is the maximum sensitivity value for silicon

- The electro-magnetic energy required to produce the photoelectric effect in silver bromide is 2.54eV
    - Using the same relationship as above, we obtain a silver bromide sensitivity of about 440 nanometers or blue sensitivity. This is the maximum sensitivity for film based sensors. Films are further sensitized in the visble and the IR with the use of chemical sensitizers.

Photodiode performance factors

Front and back lit sensors

- CCDs described thus far are designated as front lit CCDs, with the electrons illuminating the gates and moving into the silicon and producing electrons in the potential wells via the gates.
- From the QE point of view front-lit CCDs have been shown to be inefficient and back-lit CCDs have also been designed such that anti reflective coatings can be applied to prevent photon reflection (silicon has a very high refractive index, in the order of 3.6).
- Back lit CCDs look like this:



Anti-reflective (AR) coating

p-type silicon

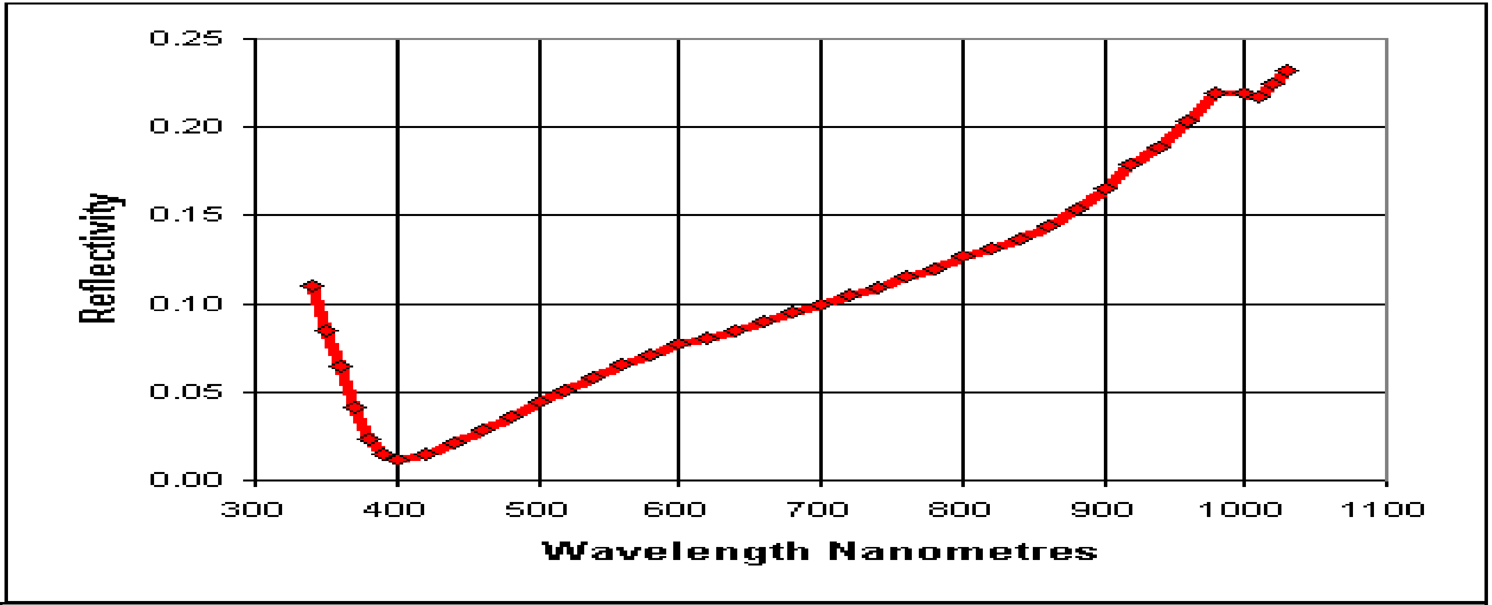
n-type silicon

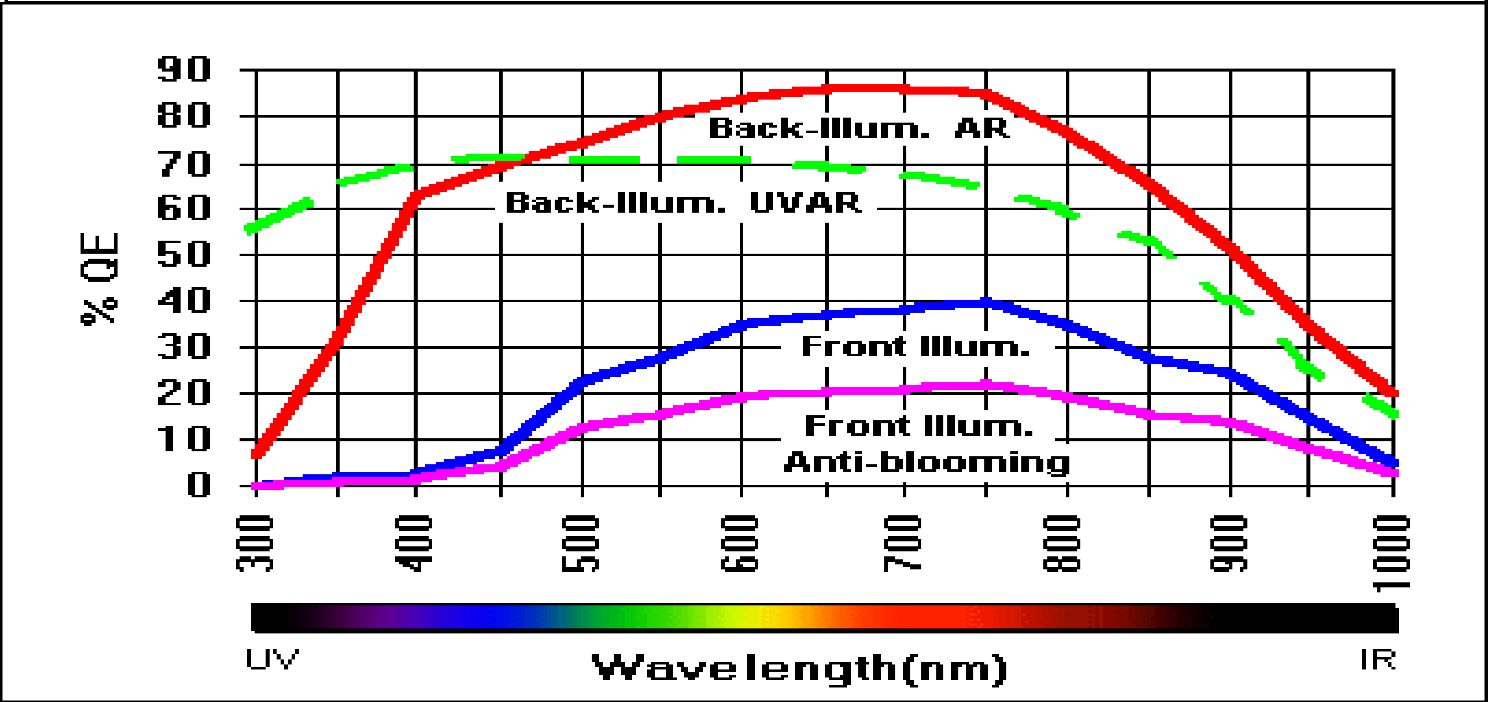
Silicon dioxide insulating layer

Polysilicon electrodes

Photodiode performance factors

QE vs λ for front and back lit CCDs





- Anti-Reflective coatings on front-lit CCDs minimize the photon loss to less than 2.5% in the IR and less than 1% in the blue-yellow end of the spectrum
- The QE differences between back-lit and front-lit thicker CCDs is shown on the second graph.

Photodiode performance factors

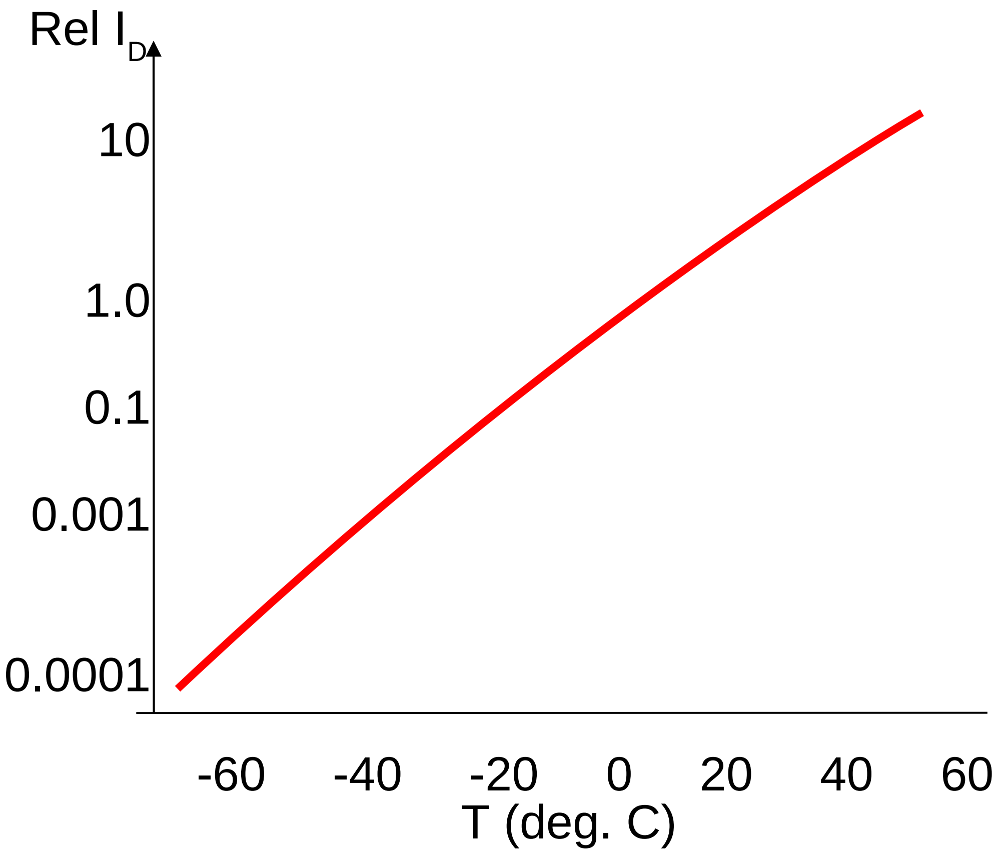
Charge Transfer Efficiency

- The fraction of charge transferred at each gate is called the *transfer efficiency* (ε). The fraction left behind or loss-per-transfer is designated by the symbol α. So, the sum of the two components is given by: ----------> $\varepsilon + \alpha = 1.0$
- Since ε determines how many transfers can be made before the output signal is seriously distorted and delayed it is a highly important figure for a CCD imager. If a single charge pulse of amplitude P_0 is transferred down a CCD register with *n* transfers, the output will be: ---------------------> $P_n = P_0 \varepsilon^n \approx P_0 (1 - n\alpha)$
- When the product nα = 1.0, then the original pulse is completely lost and distributed among several trailing pulses. So alpha must be very small where a large number of transfers are required.

Photodiode performance factors

Dark Current

- Dark current (I_D) is analogous to 'fog' for silver halide sensors; it arises from the thermal generation of electrons that accumulate in CCD elements (or produced in silver halide crystals) and add to the photo-generated signals. A typical value is 1% of the peak signal level for silicon; for silver halide sensors the 'fog' level is about 0.5%.



Since these electrons are thermally generated it follows that dark current is very temperature dependent and will follow the diode law: ----------------->

$$I_D = Ae^{-Vbg/2kT/q)}$$

Where V_{bg} is the band gap for silicon (1.12eV), A is a constant, k is the Botzmann constant (1.38054×10^{23} J K^{-1}), T is the blackbody temperature in degrees Kelvin, and q is the charge of the electron (1.6021×10^{-19} Coulombs)

Photodiode performance factors

CCD Noise

Production of non-image electrons, or noise, is an important aspect of digital image quality. Three sources of noise exist for CCDs:

I. Photon shot noise: From the random arrival and absorption of photons, charge generation is a statistical process with the signal to noise ratio at maximum when the pixels are close to maximum capacity (10^6 electrons). Photo shot noise is the square root of the signal level (given in electrons)------> $N_s = \sqrt{S}$

II. Dark current noise: As noted in the previous slide dark current noise is proportional to temperature and is generated at both exposure and readout stages. Measuring the dark current in electrons----> $N_d = \sqrt{I_D}$

III. Circuit noise : For a CCD the largest source of circuit noise is the on chip amplifier, responsible to amplifying the pixel charges to a useful level. After each pixel is read the amplifier must be reset to zero, and the uncertainty of the recovered zero level is known as the reset noise. The faster the readout the larger the noise.

The three noise types are summative and are measured in total electrons

Photodiode performance factors

Signal-to-Noise Ratio (SNR) and Dynamic Range (DR)

The signal to noise ratio for an imaging sensor is defined as the ratio between the signal and its noise, or S/N, where N is the sum of the noise contributions noted in the previous slide and the signal is the potential well electron count.The relationship is usually expressed in decibels: ----> $SNR = 10\log(S/N)$

The noise is usually a problem at low image intensity levels (as is fog with silver halide sensors) but as the charge capacity of the pixels increases so does the SNR along with the dynamic range of the image. Charge capacity would increase with a larger sensor or potential well fill capacity.

All CCD sensors have a maximum output signal (or saturation level) and a root mean square noise threshhold with voltages V_{sat} and V_{nrms} respectively. The characteristic linear response of the imager lies between these two levels (analogous to the toe and shoulder of photographic emulsions). These two levels also define the *dynamic range (DR)* of the sensor or --------> $DR = 20\log(V_{sat} /V_{nrms})$. The metric is typically in dB's. Excess pixel charge typically leads to *blooming* and is the major cause of poor highlight resolution.

Photodiode performance factors

From signal noise and dynamic range to digital numbers (DN)

The Digital Number (DN) is the parameter most people relate to regarding the signal and range from the photodiode and is the resulting value from the ADC operation. As seen many artifacts are introduced in the photon-to-electron-to-voltage-to-amplification-to-digital conversion, mostly related to types and levels of noise. These artifacts affect Dynamic Range (DR) and are important in the specifications and choice of Analogue-to-Digital-Converter (ADC). The choice of the ADC is dependent on the *effective* image information delivered to the converter. For example:

If we have a low noise CCD with a photo area of 7µm^2, electron well capacity would be about 1000X the cross-sectional area or around 49000 electrons. At a typical readout rate of 1MHz the readout noise would be 10 electrons/pixel giving a dynamic range of 49000/10 or 1:4900. A 12 bit (4096 levels) ADC would approximately match the analogue conversion information. Controlling the noise level is critical in increasing the dynamic range and utilizing the ADC optimally. If the noise of this system rose to 40 electrons/pixel the resulting DR would be 1:1225; in this case the 12 bit ADC would be creating pseudo information and a 10 bit (1024 levels) ADC would be more appropriate.

Photodiode performance factors

Linearity

A CCD sensor is capable of generating electrons in proportion the incident photons. This is an ideal imaging system unmatched by conventional photographic processes. Provided that the CCD sensor is not affected by non linear features in the amplifying circuits the output signal from a pixel is given by:

$S = kq^{\gamma} + I_D$ where k = a constant of proportionality, q = the generated charge, I_D = the dark current signal. The sensor output is linear when γ is equal to unity.

Because of various artifacts in the imaging chain the 1to1 relationship is compromised to some extent, especially in the image shadows (affected by noise) and image highlights (affected by pixel full well capacities). Specifications on the integrated sensor system linearity is typically denoted as a non-linearity %:

Nonlinearity (%) = [(Maximum Positive Deviation + Maximum Negative Deviation)/Maximum Signal] × 100

The deviations are obtained from a least squares regression between signal intensity (such as electrons or voltages produced by the sensor) and sensor integration time (exposure time)

CCD and CMOS Imaging

The traditional line on these two imaging technologies has generally been that CCDs were more adapted to higher end, higher quality image applications whereas CMOSs were used more in industrial and low resolution imaging applications. It is generally acknowledged today that this distinction is getting much more fuzzy as both CCDs and CMOSs both improve in their respective performances. Following is from Teledyne DALSA, a manufacturer of both CCDs and CMOSs on the 'state of the art' regarding the two technologies

Feature	**CCD**	**CMOS**
Signal out of pixel	Electron packet	Voltage
Signal out of chip	Voltage (analog)	Bits (digital)
Signal out of camera	Bits (digital	Bits (digital)
Fill factor	High	Moderate

CCD and CMOS Imaging

Feature	**CCD**	**CMOS**
Amplifier mismatch	N/A	Moderate
System Noise	Low	Moderate
System Complexity	High	Low
Sensor Complexity	Low	High
Relative R&D cost	Lower	Higher
Relative system cost	Depends on Application	
Responsivity	Moderate	Slightly better
Dynamic Range	High	Moderate

CCD and CMOS Imaging

Feature	**CCD**	**CMOS**
Uniformity	High	Low to Moderate
Uniform Shuttering	Fast,common	Poor
Speed	Moderate to High	Higher
Windowing	Limited	Extensive
Antiblooming	High to none	High
Biasing and Clocking	Multiple, higher voltage	Single, low-voltage

CCD/CMOS and Film Imaging

Although film based materials have been mostly been replaced by silicon based sensors (there are still some holdouts such as in the motion picture industry) there is some value in comparing the digital image sensors with an imaging technology that has evolved for over 150 years. Does film have any advantage in its imaging characteristics which may prolong its use? Is there some aspect of the film based approach that can be used to make the digital sensors even better? Let us look at some parameters:

The material: silicon vs silver halide: Surprisingly similar characteristics as semiconductors, although silver bromide requires 2.5 eV to create the photoelectric effect, silicon needs only 1.1eV. Spectral sensitivity is also quite similar in absolute terms, silicon is inherently sensitive between 300 and 1100nm while AgBr is only sensitive to about 420nm but spectral sensitivity dyes are used to extend the sensitivity to 1100nm.

CCD/CMOS and Film Imaging

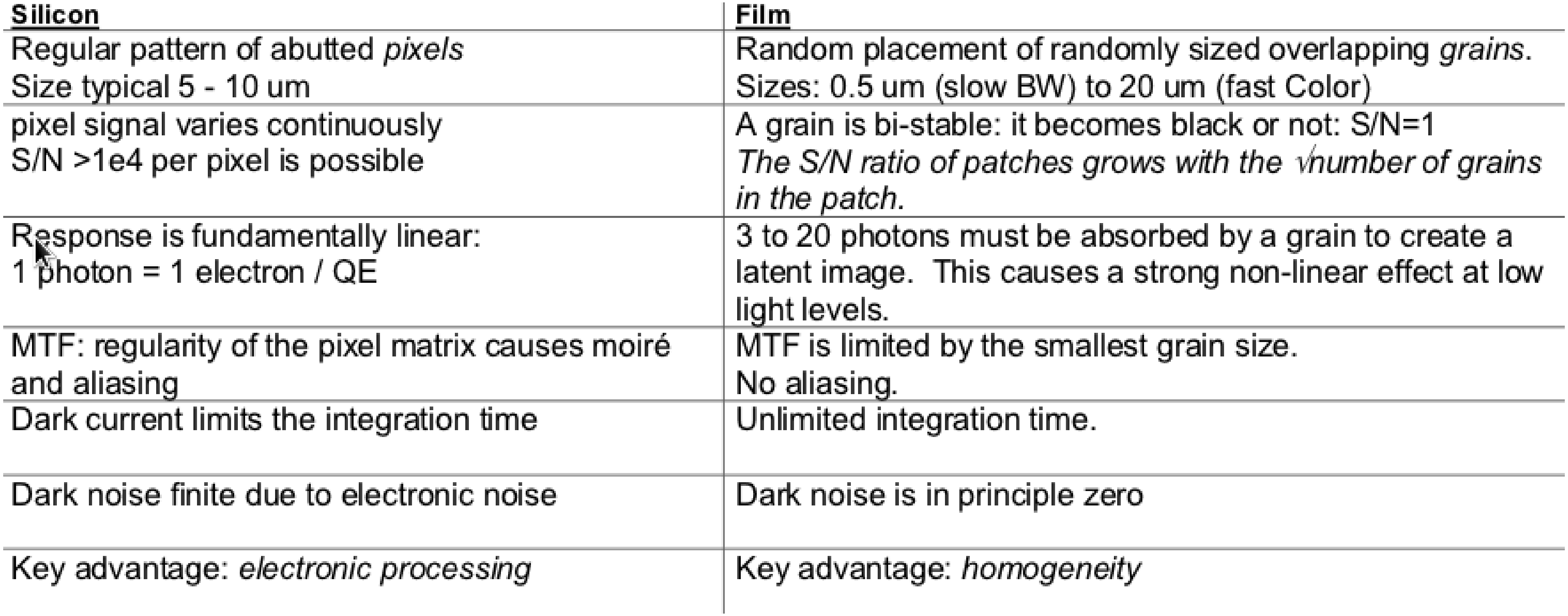
The sensor unit: The sensor unit for silicon is the photodiode, for film it is the AgBr crystal in a gelatin suspension (emulsion). Both convert photons to electrons, for silicon the conversion ratio (Quantum Efficiency) is 1:1, for AgBr it is at least 3:1 and may be upto 20:1. Photodiode sizes are usually around 5 to 10µm where as AgBr crystals range from 0.5 to 20µm

Signal processing: The photodiode analogue (electron) signal is electronically processed via amplifiers and digital converters. AgBr analogue (electron) signal represented by the latent image speck (where photo-electrons have created metallic silver) is chemically processed to amplify the signal.

Signal endpoint – the user experience: The photodiode end point is a 'pixel' bit value (8 and higher) that represents the original photons. The AgBr end point is a crystal that is either 'black' (silver) or 'white' (not developed, the 'white' crystals are removed in fixation) with the black crystals representing the original photon energy. Viewing photodiode information is typically electronic (via displays) whereas viewing AgBr crystal information is optical (levels of opacity)

CCD/CMOS and Film Imaging

A silicon/film comparison as reported by the Fill factory:



Silicon	**Film**
Regular pattern of abutted *pixels* Size typical 5 - 10 um	Random placement of randomly sized overlapping *grains*. Sizes: 0.5 um (slow BW) to 20 um (fast Color)
pixel signal varies continuously S/N >1e4 per pixel is possible	A grain is bi-stable: it becomes black or not: S/N=1 *The S/N ratio of patches grows with the √number of grains in the patch.*
Response is fundamentally linear: 1 photon = 1 electron / QE	3 to 20 photons must be absorbed by a grain to create a latent image. This causes a strong non-linear effect at low light levels.
MTF: regularity of the pixel matrix causes moiré and aliasing	MTF is limited by the smallest grain size. No aliasing.
Dark current limits the integration time	Unlimited integration time.
Dark noise finite due to electronic noise	Dark noise is in principle zero
Key advantage: *electronic processing*	Key advantage: *homogeneity*

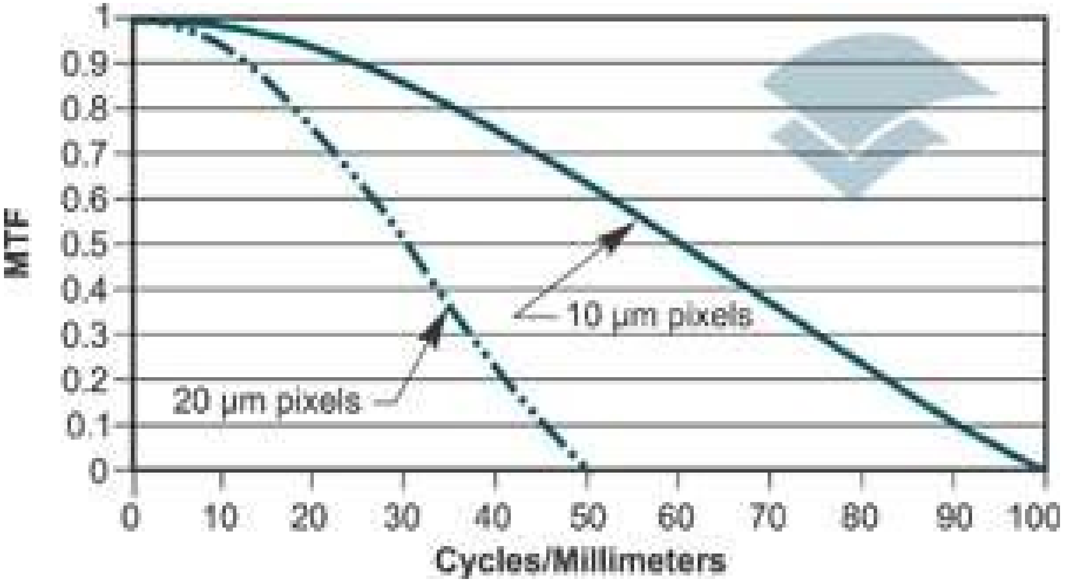
The chart does show that in some aspects film is superior to the photodiode and it may explain why, for very fine quality applications, film is still preferred. There is one parameter in this list that deserves more attention and that is the rendering of sharpness by the sensor as represented by the modulation transfer function (MTF)

CCD/CMOS
Modulation Transfer Function

The modulation transfer function (MTF) is a convenient and established metric to assess and compare the spatial resolution of CCD, CMOS and film sensors, aliasing effects notwithstanding. Just a quick refresher note of the MTF:

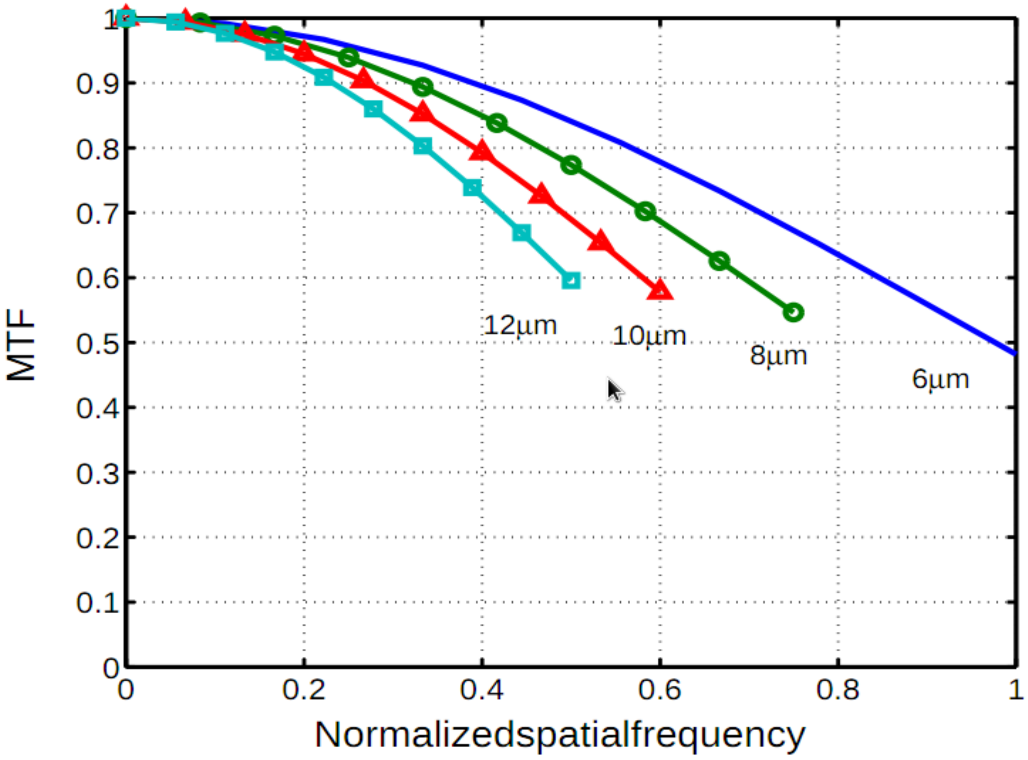
The metric is a measure of the transfer from an original object to a reproduced image of an alternating (modulating) spatial pattern of black and white bars. The pattern can be described as a sinusoidal function.

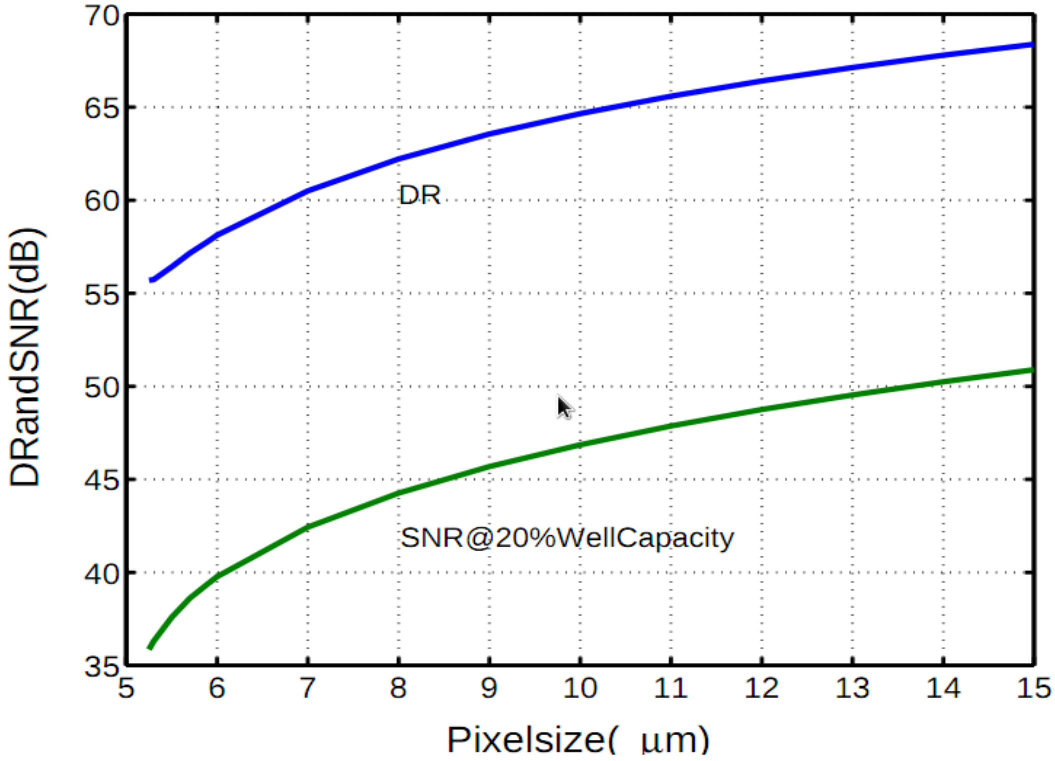
The input variable, then, is the ever increasing cycles of alternating black and white bars over a set distance (mm) and the output is the % response or output of the original pattern vs the imaged pattern.



CCD/CMOS MTF, DR and SNR

As expected the MTF performance improves as the the size of the photodiode decreases but it should be noted that this occurs at the expense of both the Dynamic Range and the Signal-to-Noise Ratio. The implication is then that the larger pixel imager, although not as highly resolving as the smaller pixel, is better at rendering image information in shadows (lower SNR) and highlights (higher well capacity).



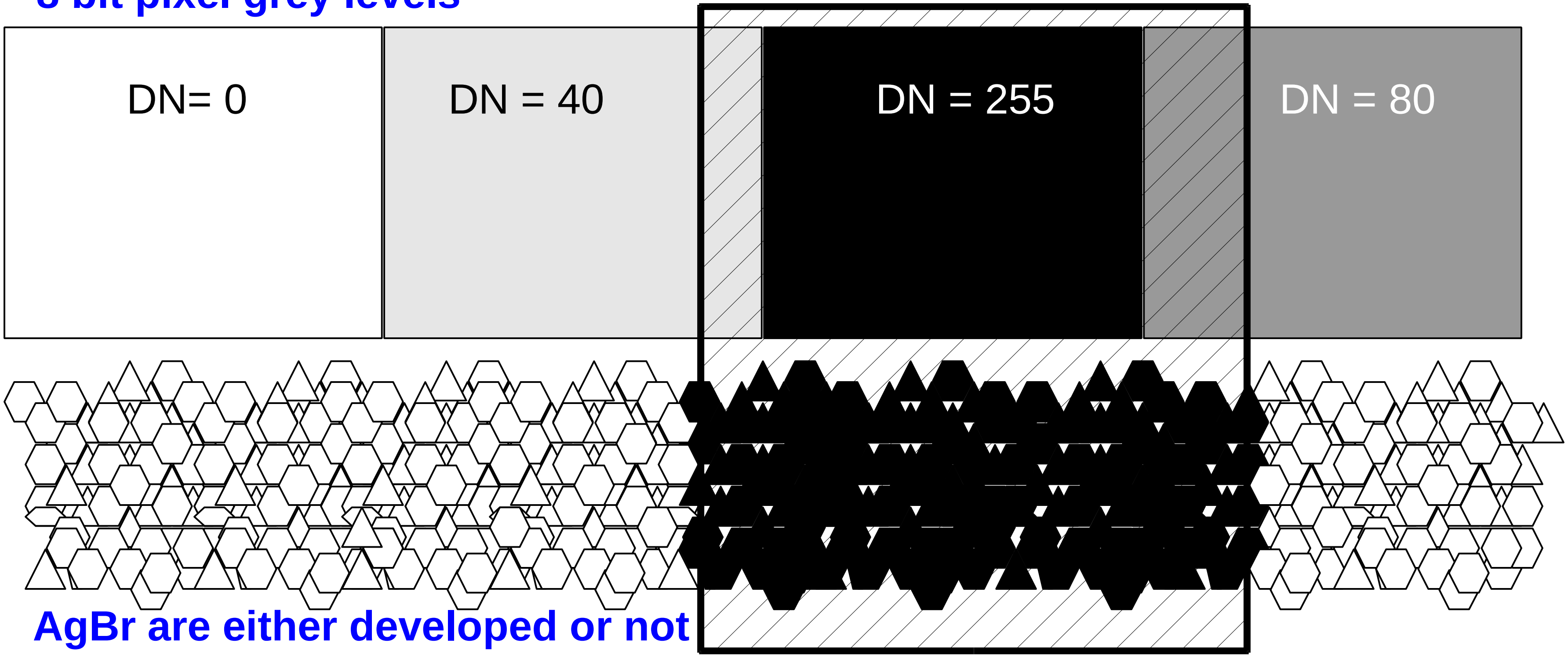


Pixel and film grain resolution

Differences at the pixel-grain level

As noted the measurement of the MTF is dependent on a bar target, its sinusoidal imaging response provides the metric for the MTF variable. But it is important to understand the details of how a very fine line is recorded by both pixels and film not only for implications on the MTF of the two media but also as a potential for future improvement. Consider the representation of a black line (hatched) 7 um wide on a 4 X 5um^2 pixel array and a film composed of 0.5um grains,what are the pros and cons these two effects?

8 bit pixel grey levels



AgBr are either developed or not

Pulling it together: comparison of two CCD manufacturers', 6µm^2 sensors

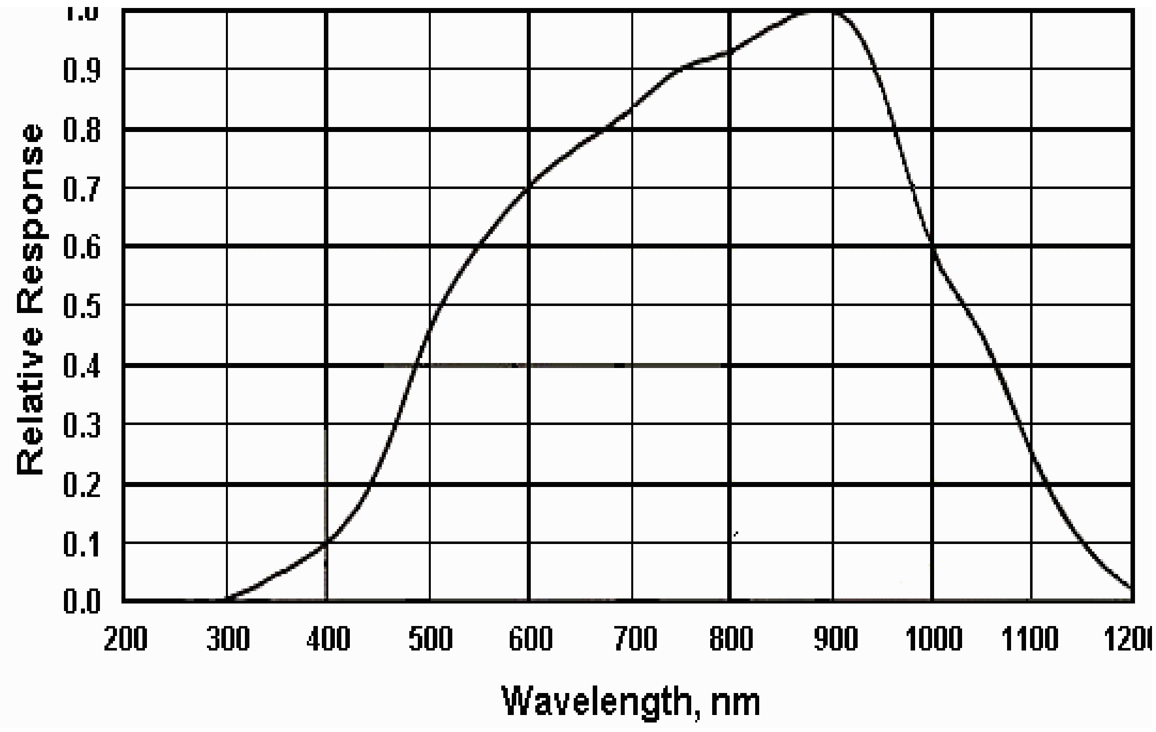
Parameter	**TeledyneDalsa**	**Kodak**
Sensor	FTF6080C	KAF-50100
Array (pixels)	6000 X 8000	8176 X 6172
QE (R,G,B)	37,31,20	22,22,16
Dyn.Rge (dB)	72.4 dB	70.2
Dark Current @60° pA/cm2	120	42
Charge Transfer Eff.	.999999	.999999
Full-well capacity (e)	50000	40300
Read Noise	--------	12.5 e
Non-Linearity	3%	5%
MTF @ 83 lp/mm	65%	----------

Photodiode Color Rendition

The Basics

By definition a CCD (a MOS) cannot represent 'color' as humans perceive color. Although silicon has inherent sensitivities from about 300nm to about 1100nm, as a sensor it can only represent the *number* of photons creating electrons and not their wavelength ie. quantity not quality. The same holds true for silver halide sensors, the process is strictly quantitative-electronic .

Silicon spectral sensitivity

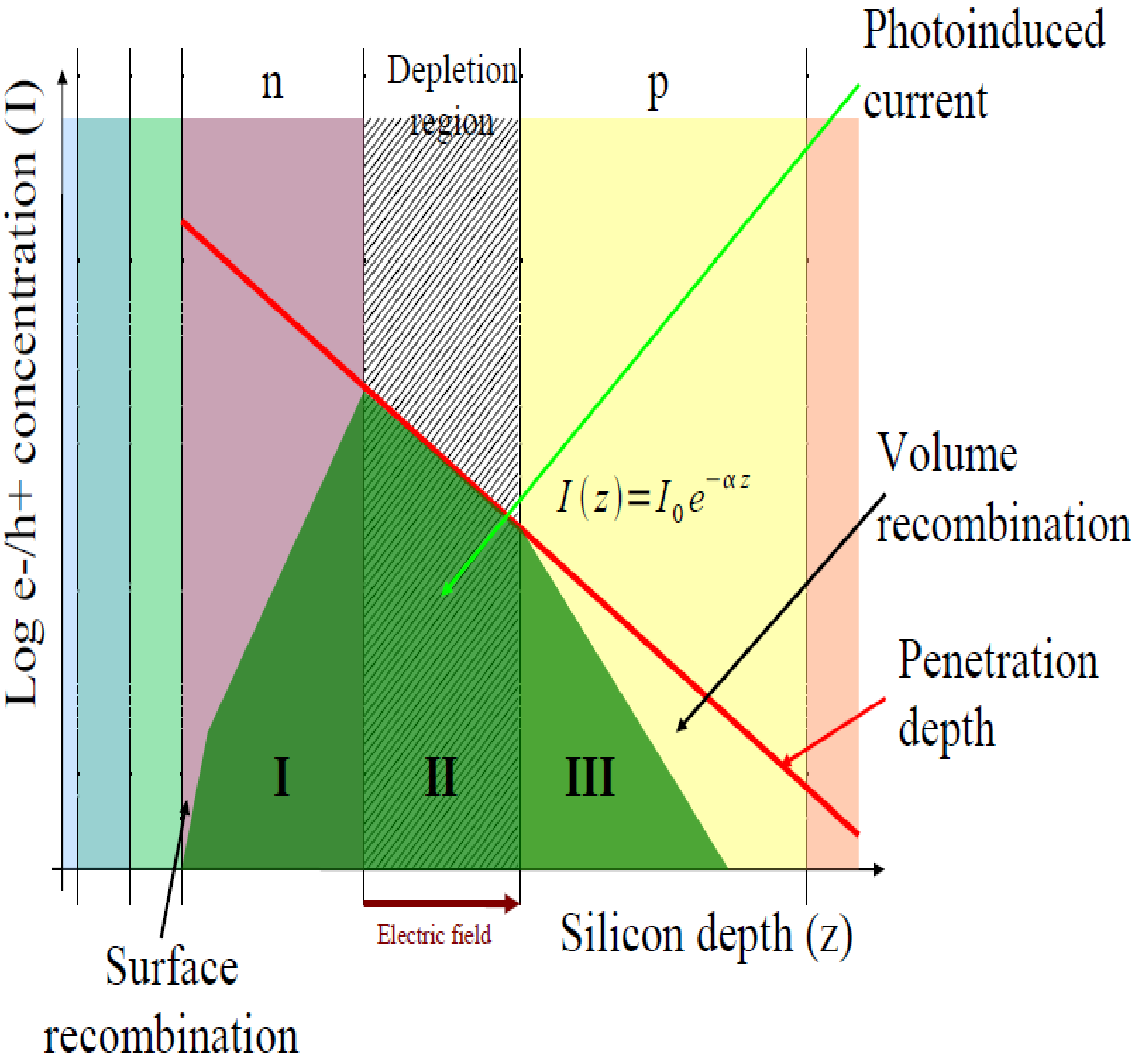


The silicon wavelength response curve on the left is a function of the material's differential absorption characteristic at different depths and the Probability of electrons-holes Recombining to nullify the Photo-electric effect. More on this later, particularly with respect to the Foveon sensor, but it is relevant to Review how the curve is obtained

Photodiode Color Rendition

Silicon's spectral sensitivity for a p-n junction

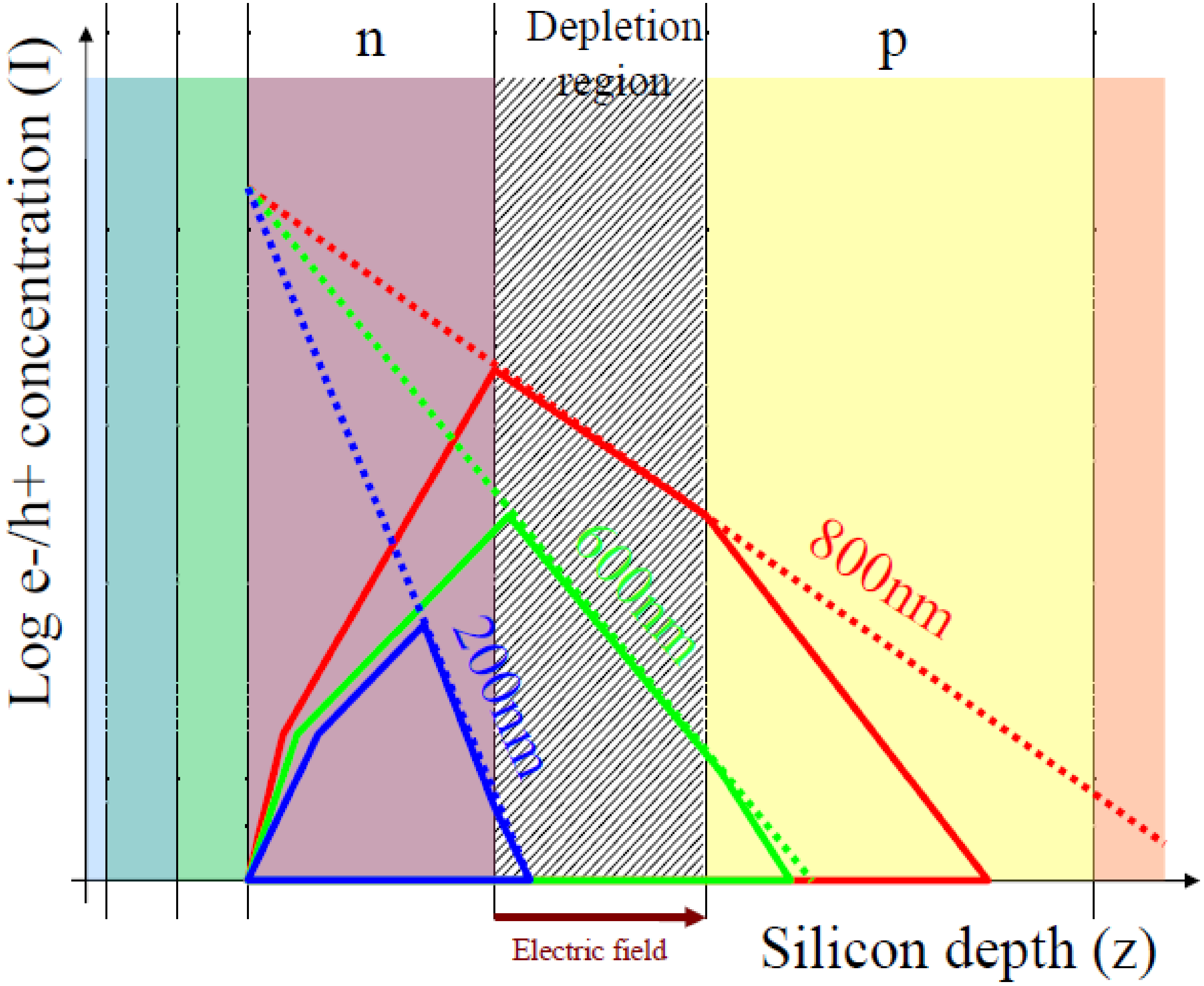
The curve in the previous slide is subject to both depth and recombination of electron-hole pairs. The red curve represents the penetration depth, the deeper you go in the silicon the less electron-hole pairs are generated. In the depletion region (region II), the efficiency is 100% as recombination does not occur, all converted photons are useful. In region I and region III, the efficiency decreases when the distance to the depletion region increases. In region I the efficiency suddenly goes to 0% close to the silicon surface.



Photodiode Color Rendition

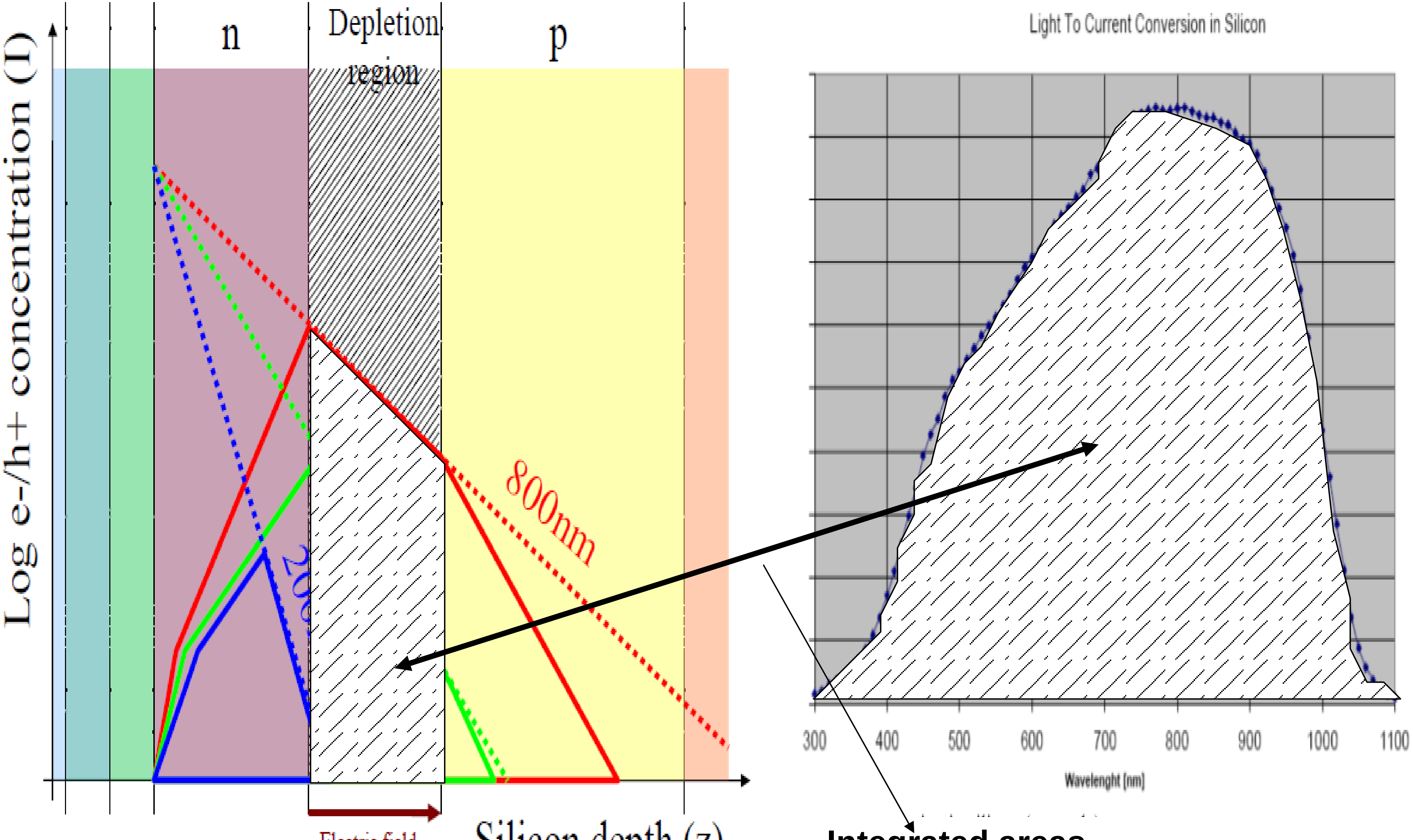
Silicon's spectral sensitivity

Integrating the areas under each of the curves in the depletion region on the right provides the general sensitivity curve for silicon. Although only three different wavelengths are shown the photo wavelength profile is continuous and is integrated between 300 and 1100 nanometers and only in the depletion region since this is where the potential well exists. See next slide.



Photodiode Color Rendition

Silicon's spectral sensitivity

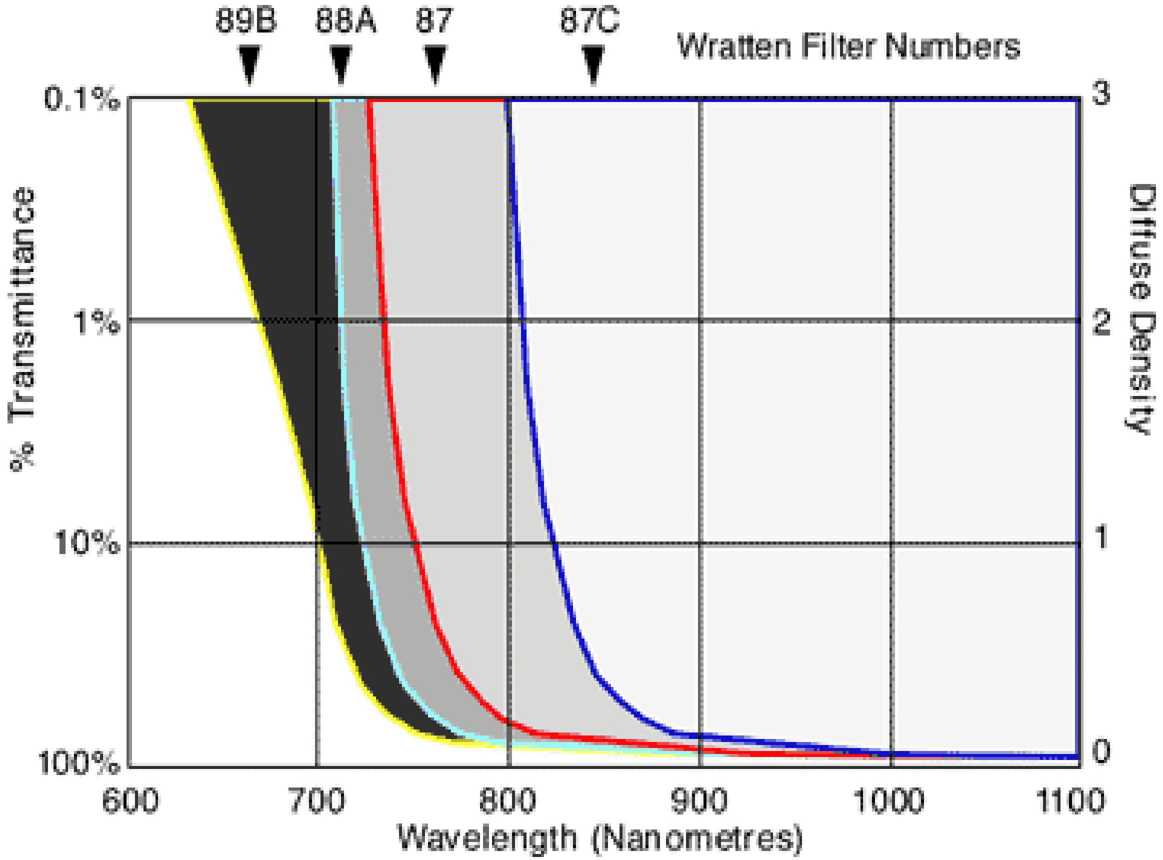


Integrated areas

Photodiode Color Rendition

Infrared 'problem'

Because silicon has an inherent sensitivity to near infrared radiation this component either needs to be eliminated for general imaging or controlled for special applications such as in remote sensing. CCD imagers are typically equipped with and IR cutoff filter which absorbs IR such as a Kodak W89B. In some cases an epitaxial layer is built in the MOS device



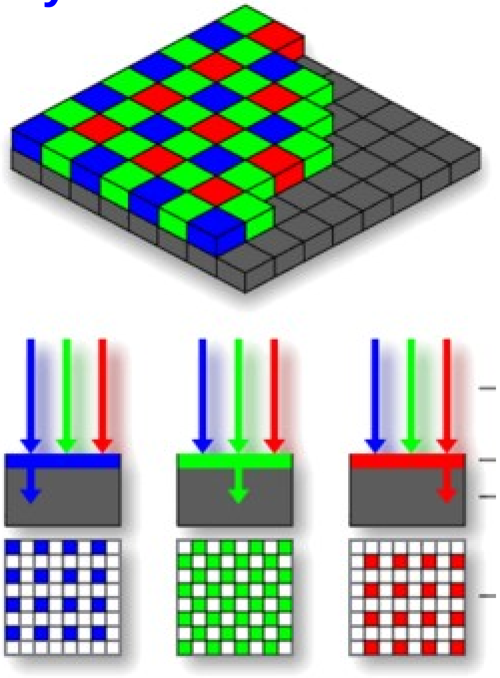
In those special cases where the infrared is desired some cameras allow the removal of the IR cutoff filter, or, in the remote sensing, the IR radiation is allocated to its own 'channel'

Photodiode Color Rendition

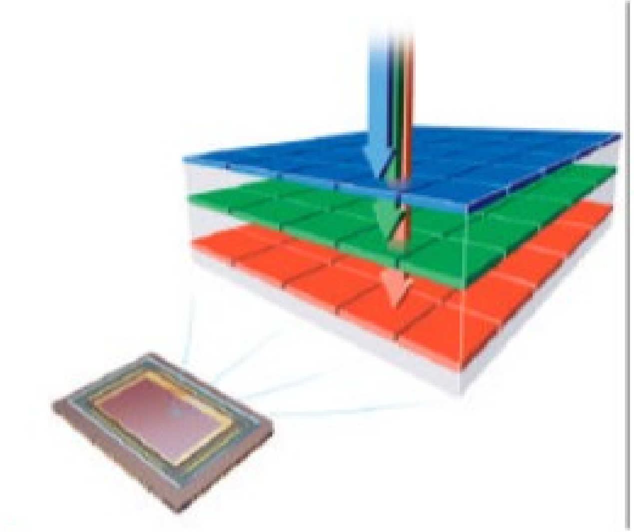
Color rendering strategies

The silicon based senor is inherently monochromatic, that is, silicon only senses the photon intensity. The photon wavelengths need to be filtered into red, green, and blue to render perceptual color. The most common filter used is the Bayer filter but other strategies such as 3 layer filtering as used in the Foveon X3 sensor and 3CCD prism filtering represent alternative techniques. All have their advantages and disadvantages and will be investigated in some detail

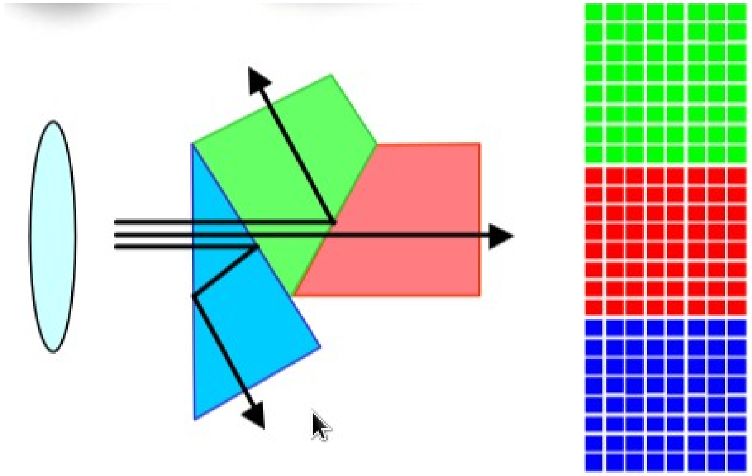
Bayer matrix



Foveon X3 layering



Prismatic or Grated separation

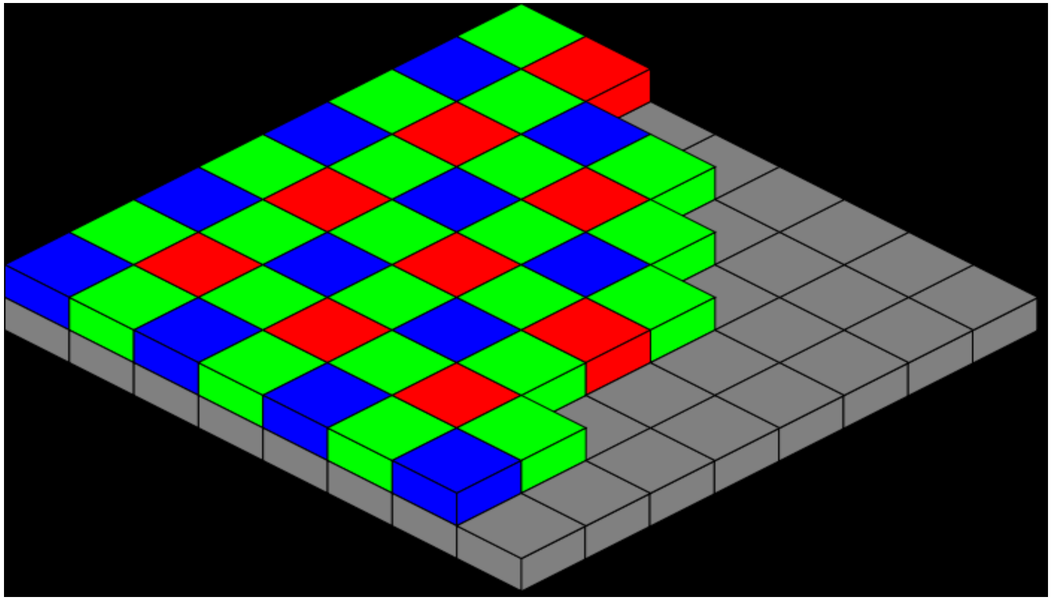


Photodiode Color Rendition

The Bayer Process

Bayer filtering is comprised of three functions:

- The initial filtering of photons into red, green and blue (RGB) wavelengths using a color filter array (CFA)
- Applying demosaicing algorithms to reassemble the fragmented Bayer matrix
- Interpolating RGB values for each pixel



The Bayer filter, created by Bryce Bayer (Kodak) is designed to reproduce color as sensed by the human eye. The eye contains more rod cells than cone cells and rod cells are more sensitive to green light; the Bayer matrix contains twice as many green filters. Thus, Bayer images will have inherently more true green information (photons) than either red or green. The grey strata in the image represents the CCD MOS device and operates as per MOS and CCD principles.

Photodiode Color Rendition

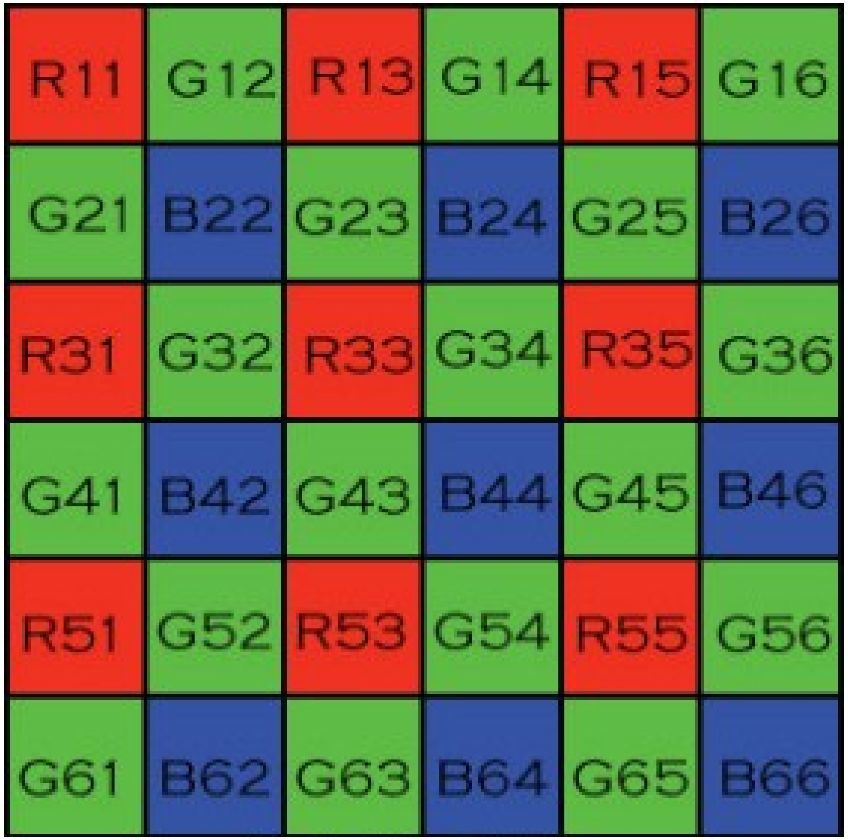
The Bayer Process: Demosaicing

Image information filtered by the Bayer filter and collected by the CCD is generally considered to be in raw format, that is, it represents the true information content collected by the sensor. It is equivalent to the negative in conventional imaging. As a result of Bayer filtering each pixel will only contain one value for each of the Red, Green or Blue. It is the job of demosaicing and interpolation algorithms to 'create' the missing color component for each of the pixels. Along with attempting to calculate the 'coorect' missing value, the algorithms must ensure that anomalies such as chromatic aliasing, zippering, purple fringing etc. are avoided. Typical demosaicing algorithms include:

- Pixel Doubling
- Bilinear and Bicubic Interpolations
- Gradient Based Interpolation
- High Quality Linear Interpolation
- Adaptive Homogeneity Directed Interpolation

Photodiode Color Rendition

Demosaicing example: Reconstructing the Pixel RGB value using a simple Bi-linear method



R11	G12	R13	G14	R15	G16
G21	B22	G23	B24	G25	B26
R31	G32	R33	G34	R35	G36
G41	B42	G43	B44	G45	B46
R51	G52	R53	G54	R55	G56
G61	B62	G63	B64	G65	B66

Pixel R33 (red pixel):
Red = R33
Green = (G23+G34+G32+G43) / 4
Blue = (B22+B24+B42+B44) / 4

Pixel B44 (blue pixel):
Blue = B44
Green =(G33+G35+G53+G55) / 4
Red = (R33+R35+R53+R55) / 4

Pixel G43 (Green in a blue row):
Green = G43
Red = (R33+R53) / 2
Blue = (B42+B44) / 2

Pixel G34 (Green in a red row):
Green = G34
Red = (R33+R35) / 2
Blue = (B24+B44) / 2

Photodiode Color Rendition

Issues with Demosaicing

A number of artifacts were noted earlier (chromatic aliasing, zippering, purple fringing) and we can add to this list other effects such as blurring, banding, grid effects, false color (not associated with IR). Most of these are dealt with some interpolation process but as expected the perfect interpolator has yet been devised!

Essentially the problem is one of missing information. So, can a sensor that captures the missing information be engineered? With the cost and efficiency of MOS devices and storage becoming more affordable and effective, designs to capture the RGB values at the the time of exposure (as with film) have been developed.

Two technologies associated with capturing the RGB value at time of exposure are:

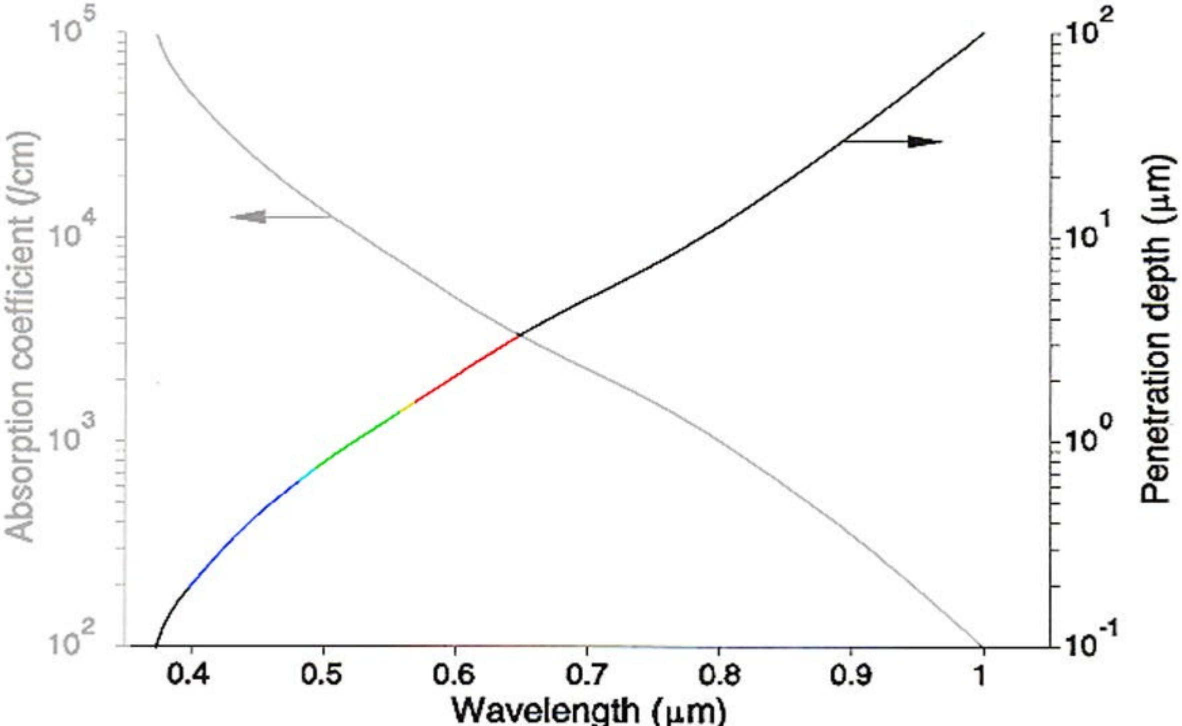
- Layered Foveon X3 technology, and
- Beam splitting 3 CCD technology

Both these approaches eliminate the process of demosaicing.

Photodiode Color Rendition

Utilizing silicon's spectral sensitivity characteristics with layered RGB filtration

Layered filtration (as with film) uses the inherent differential depth sensitivity of silicon to partition out photons of different energies and wavelengths. As noted earlier silicon has an effective light sensitivity between 300 and 1100 nanometers but electrons and holes are produced at different depths in the silicon. This was alluded to in the discussion on back-lit CCDs. Let's investigate the theoretical background:



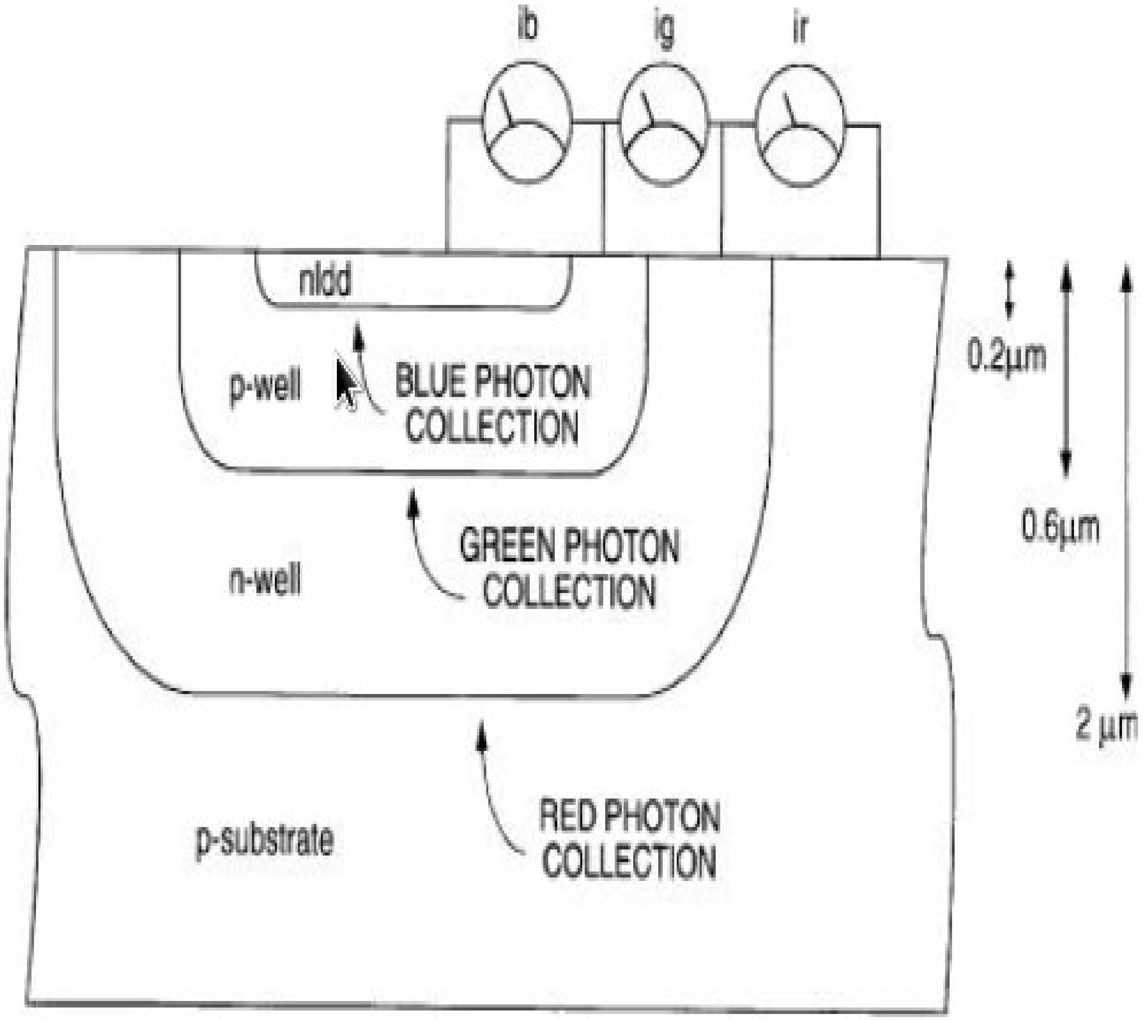
The Beer-Lambert Law will serve us well in relating transmissivity and absorption through a substance, in our case silicon.

$I(z) = I_o e^{-\alpha z}$, where z is the silicon depth, I is the light intensity and α is the absorption coefficient.

Photodiode Color Rendition

Silicon's spectral sensitivity characteristics and the Foveon X3 Sensor: The triple-well photodiode

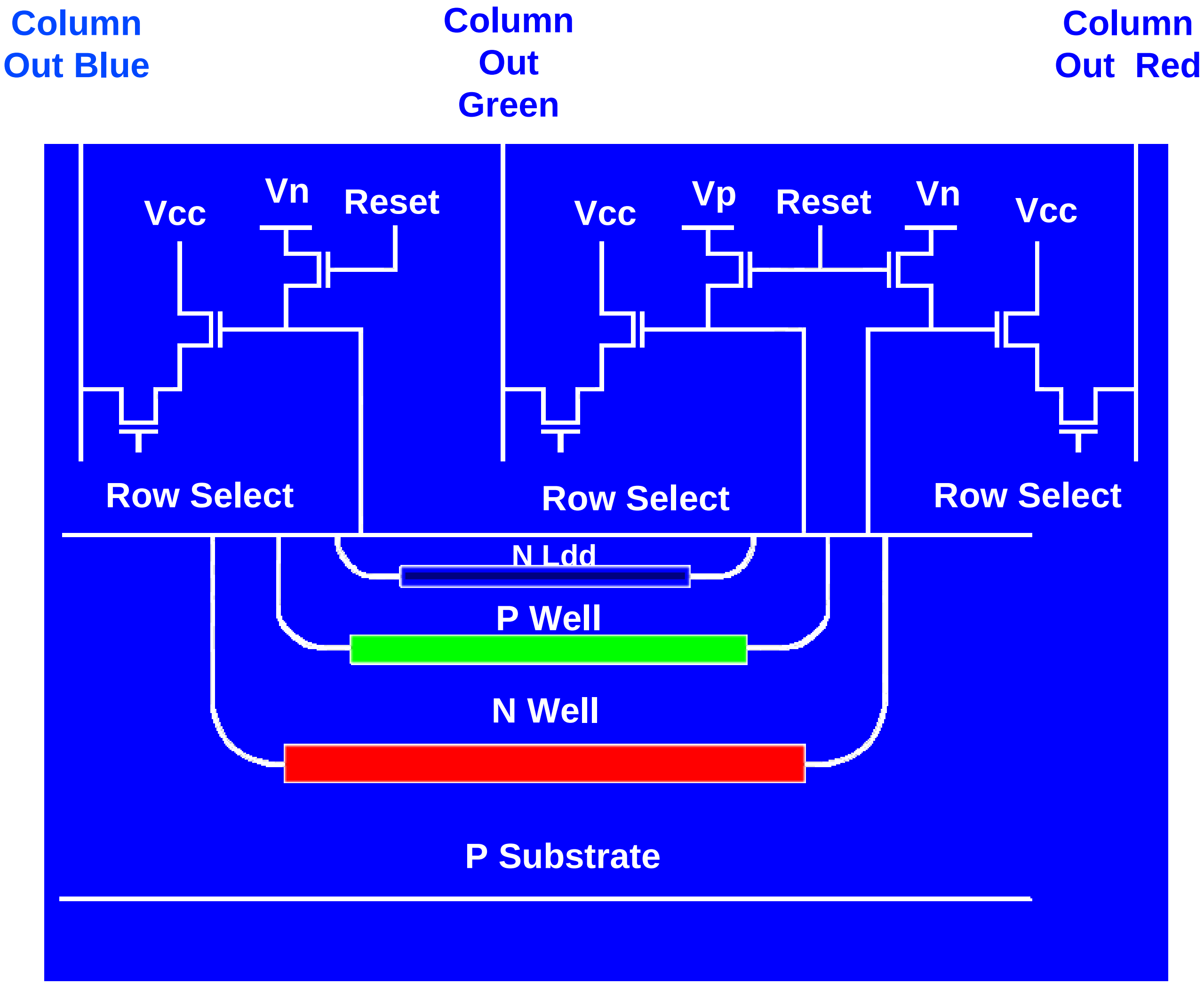
- The Foveon X3 sensor employs a triple-well strategy to capture and segregate the blue, green and red photons and their electrons. **Based on the differential wavelength depth dependent absorption of silicon**, the blue photo photons are absorbed and 'welled' at the shallowest junction, the green at middle junction and the red at the deepest junction.



Photodiode Color Rendition

Silicon's spectral sensitivity characteristics and the Foveon X3 Sensor: CMOS design

The Foveon X3 sensor is not a CCD, that is, it does not use charge coupling to transfer the electrons produced to a collection register. It employs the CMOS design to transfer coverted charges to voltages immediately from the pixel. The pixel sizes tend to be larger with CMOS devices but the gain is usually offset by speed enhancement



Photodiode Color Rendition

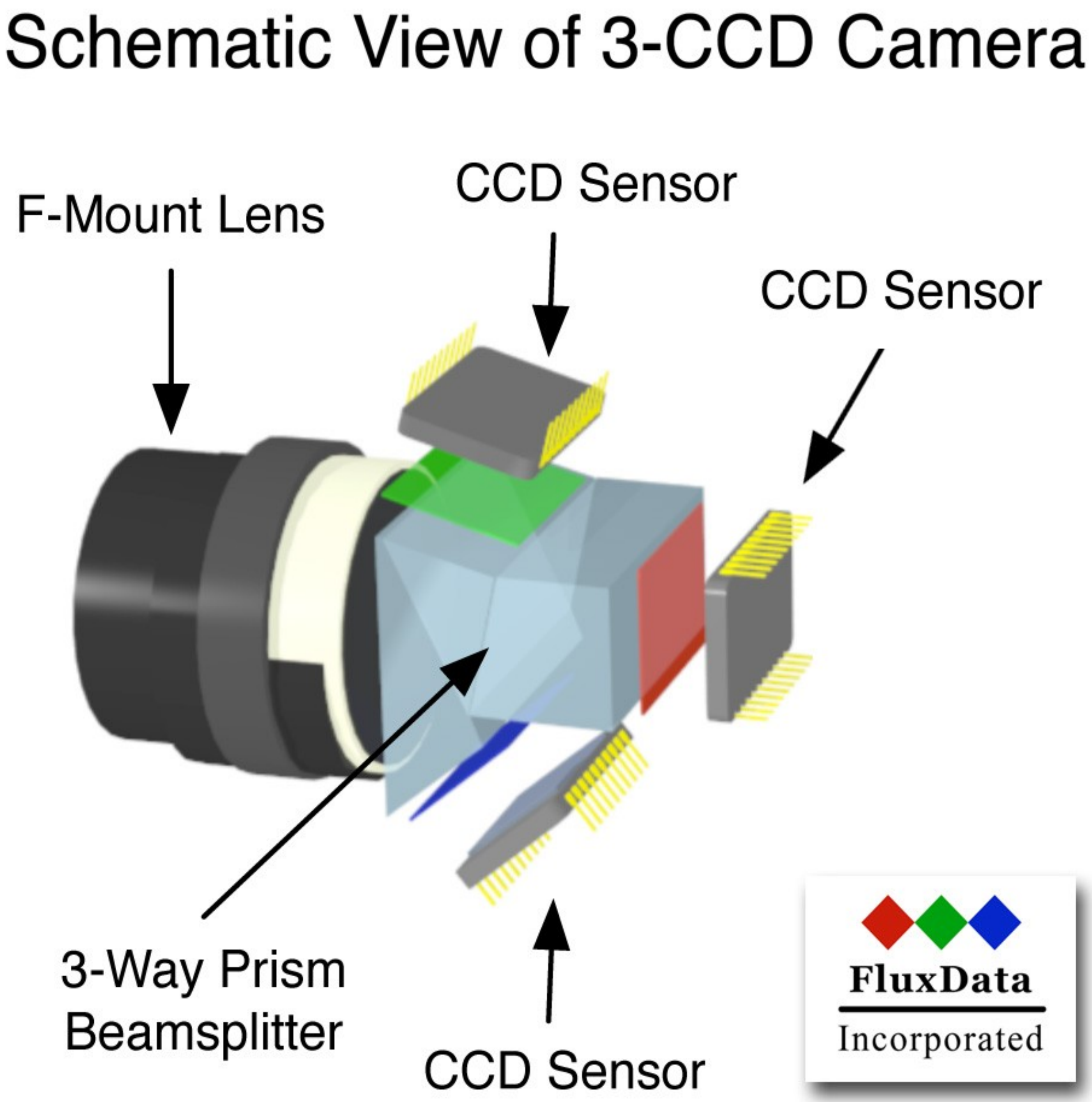
Prism filtering: the 3 CCD approach

Often denoted as 3-chip imaging as each chip is used to capture one of the three primary colors.

All 3-chip systems partition out the light via prisms or diffraction gratings to produce components of red, green, and blue.

Each of the components are used to illuminate a full sensor array without any filtration, thus enabling the use of *all* the pixels for each color.

A registration of each color component recombines to form the RGB image



Future of Imaging Materials

Where to from here?

Materials

Base Material: Silver halides have been the primary sensing material for over 150 years and have generally been repiaced by silicon starting some 40 years ago. Other compounds are being used for specialized applications such as extended infrared sensitivity but do not have mass application as did AgBr and that silicon has today. Research is active in using doped diamond as one such material (undoped diamond has an energy gap of 5.45 eV and is an insulator, not a semiconductor); from Kraft (2007), Int. J. Electrochem. Sci., 2 (2007) 355 – 385.

Doped-diamond electrodes display also interesting photoelectrochemical properties [56-58]. Since diamond has a very wide bandgap, visible and long-wavelength ultraviolet (UV) radiation should not be able to excite electrons from the valence into conduction band. Nevertheless, some studies show significant photocurrents even with subbandgap illumination [35, 56], presumably due to impurity or surface states within the bandgap. Fujishima and coworkers [57] could show that on highquality diamond electrodes with very low nondiamond carbon content only irradiation with suprabandgap illumination is able to excite electrons into the conduction band... Diamond based sensors would improve electron leakage and provide faster signal response.

Shallow Junction Photonics:SiOnyx (Black Silicon) uses ultra fast laser technology to enhance the quantum efficiency of thin films of silicon. SiOnyx devices exhibit ground breaking advantages in low light detection, infra red imaging and ultimately a better, lower cost solar cell.

Future of Imaging Materials

Where to from here?

Full-well Capacity

Full well capacity improvements: Improving well capacity in CCDs and CMOSs addresses the issue that photodiodes have with signal saturation or the maximum number of electrons that be contained in the potential well following light exposure or integration. It is an attribute commonly reported in sensor specifications as number of electrons with the electron value decreasing as the size of the photodiode also decreases.

Some of the photodiode/CCD/CMOS design techniques to improve this parameter include:

- Omnivision: reduces a transfer gate sidewall spacer closest to the photodiode. The abrupt junction of pinning layer is achieved by reordering the implanting pinning layer step to be after formation of sidewall spacers. Omnivision has also implemented using copper wafers on silicon that allow about a 45% increase in full well capacity.
- US patent US20110101420: the circuit includes two transfer gates and a capacitor to store charge between the transfer gates.
- Multiple p-n-p-n junctions have been proposed to increase the size of the PD region for charge storage and therefore the full-well-capacity. With optimized implants and layout, a full-well-capacity increase of 50% has been demonstrated without increase in pinning voltage or image lag. Other techniques for increasing the full-well-capacity have also been suggested. For example, it has been proposed to use solid source diffusion (SSD) or plasma doping to form ultra-shallow junctions.

Future of Imaging Materials

Where to from here?

Noise and dynamic range

Improving noise and the signal-to-noise ratio leads to major quality benefits in digital imaging and significant research effort is invested by sensor manufacturers to address this parameter. Some of the noise parameters have physical constraints such as the stochastic nature of photon shot noise or the thermal dependence of dark current noise. Some are technology dependent such as the circuit noise and read out noise .

- E2V: Electron Multiplying CCD (EMCCD) - The combination of the very high quantum efficiency of back illumination with electron multiplication leads to extremely sensitive devices capable of efficient single photon imaging at high frame rates. A prototype EMCCD sensor for a Light Detection and Ranging (LIDAR) instrument has been developed.
- SNR reduction by image averaging – Statistical algorithms for improving the SNR ratio are numerous, a particularly promising capitation is the use of Order Statistics to further refine the image signal and the dynamic range

Future of Imaging Materials

Where to from here?

Pixel Size

The smallest commercial sensors today are in the order of about 1.1 micrometers, with CMOSs generally smaller than CCDs. But, smaller pixels may not be the ultimate goal for all applications. There is a fundamental discord in the size objective: although smaller pixels equate to better resolution and image MTF, they also contribute to lower dynamic range and Signal-to-Noise ratios and of course lower light sensitivity. Unless there is a radical change in the physics of this relationship we may need to be content with an *optimum* pixel size, depending on the application. In remote sensing that optimum seems to be around 6microns, with significant deviations, in professional photography, the smaller pixels are still being striven for. Mass consumer video applications tend to favor the smaller pixel sizes for compactness. DSLRs and photogrammetric applications are concerned with high DR and SNR. In these type of applications larger overall sensor size (optical format) is desirable with newer designs favoring the conventional film sizes.

$$OF = p\sqrt{w^2 + h^2}/16000$$

p=pixel size in microns
w=# of pixels width
h=# of pixels height

Future of Imaging Materials

Where to from here?

Architectures

The image sensor has seen many design improvements over the past 40 years. Just to recap some of the most influential changes and the gains made with each successive design:

- Linear vs Area arrays: Linear systems are simpler designs but for more specialized applications, often used in remote sensing platforms, area arrays are complex but more aligned with the conventional 2 dimensional image and enjoy more mass application.
- Surface vs Buried Channel CCDs: The buried channel improves the efficiency of the charge coupling process in CCDs with less electrons interacting with surface and interface states.
- The 'PINned' photodiode: An intrinsic semiconductor (I) is inserted between the basic p-n junction of a semiconductor, hence, the P-I-N structure, improving the QE of the photodiode.
- Front-lit vs Back-lit CCDs: QE improvements of around 50% are realized with back-lit CCD assembly.
- Passive and Active CMOSs: APS has improved the speed and performance of CMOS technology significantly.
- CCDs vs CMOSs: CCDs better overall quality and CMOSs being faster and more efficient in processing the digital signal due to integrated pixel design. The two technologies slowly merging.

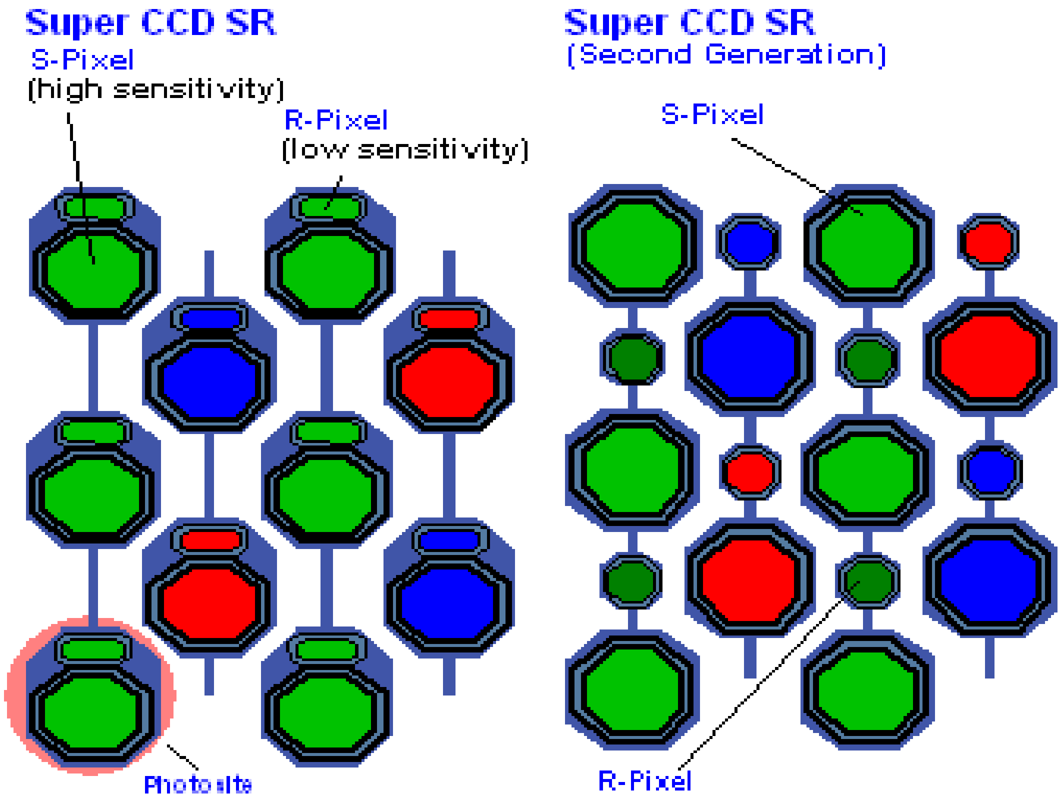
Future of Imaging Materials

Where to from here?

Improvements In CCDs

Research in to better architectural designs is ongoing. As the previous slide implies larger arrays may become the norm in the future but what about new designs? Following is where some of the current development is focused:

Super CCDs: The Super CCD platform combines the simultaneous benefits of high resolution, high sensitivity, and wide dynamic range from a single sensor. It incorporates hexagonal S and R photodiodes to maximize sensitivity (from the S pixel) and resolution (from the R pixel) to optimize the characteristics of larger and smaller pixel sizes.



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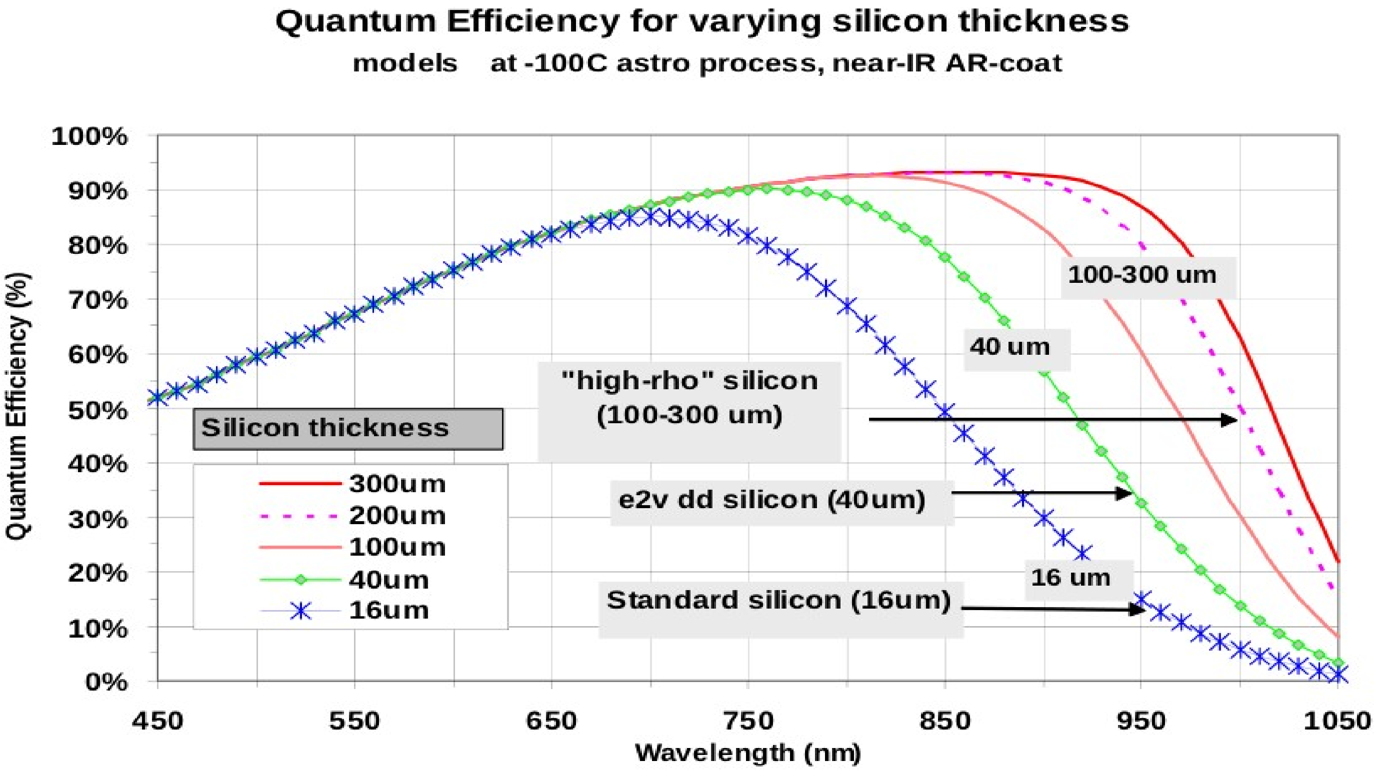
Future of Imaging Materials

Where to from here?

Improvements In CCDs

Electron Multiplication CCD (EMCCD): With the use of a gain register photon events above the noise level can be detected and amplified to provide low illumination image profiles, useful in astronomical (weak signals) and remote sensing applications (shadow areas). The ANDOR Technology site provides some good background on the technology: http://www.emccd.com/what_is_emccd/emccd_tutorial/Q1_What_are_Electron_Multiplying_CCDs/

Detection Efficiency: Improving the QE Profile in the Near Infrared where silicon Naturally becomes Less sensitive. E2V's Strategy is in thickening Silicon (high rho). Of Major interest to remote Sensing applications



Future of Imaging Materials

Where to from here?

Improvements In Films

Film Doping: Film material, although largely supplemented by CCDs and CMOSs, still does have a niche market in areas such as artistic photography, motion pictures, aerial photography and some biomedical applications. The wide dynamic range capability of color films (1:4096) plus the inherently larger data capture and resolution potential of the film medium (some 200Mpixel equivalent for 8X10 or 9X9 in. negatives).

The most significant improvement is in the silver halide semicondutor QE and the dramatic change its film speed. The use of a doping process can increase the speed of a silver halide film by 5 times7. In present emulsions as much as10 photons of light is needed to produce a developable latent image. Using formate ion (HCO2) as a 'hole scavenger” dopant, will allow only 2 photons to produce a developable latent image. This will enable the use of smaller crystals producing higher speed. The result will be a fine-grained, high resolution film 5 times faster than the highest resolution film availabe today. This doping can be applied to both black and white and color films resulting in dramatically new film emulsions than are presently available (Brandes, Agfa Corp.)

Future of Imaging Materials

Where to from here?

Discussion

Consider silver halide based technology and the improvements over its 150 year use. Consider silicon based technology and the improvements over the past 40 or so years. Questions to consider:

- How much better can the current technologies become? Base your responses on the variables presented. Point out the scope of the improvements and what advantage they will provide for imaging applications. For silicon consider CCD/CMOS performance factors, for silver halides consider their digital adaptation.

- Speculate on alternative imaging materials and processes and their future applications. Two have been outlined (diamond and black silicon), are there others? What are the quantum conditions in materials that are required for photon-electron pair conversion? Can quantum energy be used directly without resorting to electronic processes as is the case in silver halide and silicon?

- Optional: Although LiDAR technology was not addressed consider the potential of this technology as a *full fabric photon flux and sensing* imager in its remote sensing realm and, more importantly, as a mass consumer imaging device.