

# A Literature Review on Passivation of HgCdTe (MCT) Infrared Detectors

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**Abstract:** *This review examines surface passivation approaches for HgCdTe (MCT) infrared detectors, focusing on challenges associated with surface defects, thermal instability, and interface degradation. Common passivation materials, including ZnS, SiO<sub>2</sub>, SiN<sub>x</sub>, anodic oxides, sulphides, fluorides, and photochemical oxides, are comparatively evaluated in terms of interface quality, thermal stability, dielectric behaviour, and chemical durability. The analysis indicates that while existing passivation methods offer partial benefits, significant limitations remain. Based on lattice compatibility, thermal expansion matching, optical transparency, and mechanical stability, CdTe emerges as a promising alternative passivation material for improved MCT detector performance.*

**Keywords:** HgCdTe; MCT; infrared detectors; surface passivation; ZnS; SiO<sub>2</sub>; SiN<sub>x</sub>; anodic oxides; photochemical oxides; CdTe; semiconductor interfaces.

## 1. Introduction

The fabrication of stable, high-performance HgCdTe infrared detectors critically depends upon the surface electrical properties of MCT. Surface passivation of HgCdTe is particularly difficult and offers a major challenge in view of the complex chemistry and temperature sensitivity of the material. As mentioned earlier effective passivation of the semiconductor surface is a critically important step in fabrication technology. The passivant film must apart from sealing the material both electrically and chemically, serve as a mask against implantation or diffusion into the semiconductor, provide a surface over which electrical connections can be made between different devices in a planar configuration and act as an antireflection coating. In case of MCT photodevices, the passivant must protect the semiconductor material from humidity and other contamination. It must also stabilise the material chemically since Hg would otherwise diffuse out especially in a low pressure and high-temperature environment. First of all, the passivant must control the surface leakage currents, which necessitates high-quality passivation. The passivating layers for MCT photodevices must, in general, satisfy the following criteria:

The passivating layer must

- 1) be good insulator and adhere well to MCT.
- 2) be stable, as a function of time and against the atmosphere.
- 3) not be attacked by chemicals necessary for fabrication process
- 4) be sufficiently non-porous so that atmospheric gases cannot diffuse through it and attack the HgCd, Te material.
- 5) produce an interface which is sufficiently electrically inert so that it does not degrade the operation of the photodetector in an unacceptable way.

It is however, not so easy to satisfy these conditions. The following two difficulties are involved because of the nature of the MCT material. Physical and chemical treatment made on surface leads to stoichiometric changes and mechanical damage. Physical and chemical treatments made on MCT surface lead to stoichiometric changes and mechanical damage. The standard etching process using bromine in

methanol depletes the MCT surface of cations, leaving a thin layer of activated Te rich in dangling bonds (1-2), this eventually leads to air grown oxides of tellurium (TeO<sub>3</sub>) at the surface (3-4). Because of the intrinsic fragility of the material lapping produces a damage which may extend into the bulk as much as twenty times the grit size for a 1 μm grit (5). Stress from lapping and cleaving often causes a migration of Hg, resulting in non-stoichiometric surface (6). In vacuum, at a temperatures ~100-200°C Hg diffuses out from the surface in minutes. At room temperature too, mercury depletion takes place in vacuum through at slower pace (7). The extreme susceptibility of the MCT material to physical and chemical treatments is related to the inherent weakness of the Hg-Te bonds (8). It is also important to realise that the mechanical properties of MCT at room temperature are similar to those of silicon (9) above 1000K. Thus, one can easily anticipate the possibility of mechanical damage in the surface region and the effect of this on the properties of device surfaces. The instabilities of the MCT lattice and the surface leads to strong MCT-passivant interaction with the result that the insulators interface in MCT is more complex than in the common semiconductors. Thermal instability also increases at temperatures exceeding 80-100°C, which necessitates near room temperature processing for MCT. Because of thermal sensitivity of MCT, any high temperature passivation process such as thermal oxidation, a process most popular in silicon technology, is at once ruled out. To overcome the problem of thermal instability, physical and chemical sensitivities of MCT, different materials have been tried as passivant layers. The passivants considered most effective till date are listed below:

- 1) Deposited insulators, such as zinc sulphide, silicon dioxide or silicon nitride.
- 2) Native oxides, sulphides or fluorides.
- 3) Combinations of the above two dielectrics In this type SiO<sub>2</sub> or ZnS are deposited over native oxide film of thickness 50-150 Å.

The various passivating layers that have been tried to passivate HgCdTe are shown in fig. 1

## 2. Literature Review

The literature review of the various passivation technologies used for Hg<sub>1-x</sub>CdTe:

### Zinc Sulphide (9-13):

Zinc Sulphide is the first insulator that was used on MCT for fabrication of MIS structures ZnS is deposited on MCT because of its compatibility with the MCT lattice, excellent properties and dielectric strength Both have zincblende structure like other II-VI materials, with well matched lattice parameters of Hg<sub>0.8</sub>Cd<sub>0.2</sub>Te and ZnS at 6.464Å and 5.409Å respectively. For passivation purposes ZnS is deposited by resistive heating evaporation under a vacuum of  $1.5 \times 10^{-6}$  Torr at a relatively slow rate or by electron beam evaporation. Deposition by magnetron sputtering improves adhesion but has the probability of introducing damage to the MCT surface ZnS deposition on freshly etched MCT substrates forms high quality interface with very low fixed surface charges. Fixed charges can be produced by exposure to blue or ultraviolet light which can be controlled by annealing in dark. The adhesion between ZnS and MCT is excellent on freshly etched HgCdTe surfaces. Adhesion problems and interfaces with inconsistent electrical properties are observed on surfaces which have been exposed to chemicals during processing steps. The MCT-ZnS interface exhibits instability under temperature cycling at 80-90°C. It is a poor insulator compared with SiO<sub>2</sub> The ZnS films are relatively inert sensitive to water and can be etched with concentrated HCL. Its mechanical properties are also not very reliable and it can crack during ultrasonic bonding on overlaying metallization structures. The bulk resistivity is high but inferior to SiO<sub>2</sub>. Dielectric constant of ZnS is  $\epsilon = 7.45$ , index of refraction  $n = 2.15$  at 1 $\mu$ m and it has energy gap  $E = 3.6\text{eV}$ . Considering all its characteristics ZnS can be used as a passivant for photodiodes, insulator for two-level metallization - structures, as an implantation mask and for encapsulation purposes.

### Silicon Dioxide (14-20):

Low temperature deposition of SiO<sub>2</sub> is carried out by the CVD photox process. In this process SiH<sub>4</sub> is made to react with atomic oxygen and SiO<sub>2</sub> deposits on MCT substrates. MCT is maintained at temperatures of 40-100°C. There are various techniques for obtaining atomic oxygen which is reactive even at low temperatures (i.e. 40-100°C). The photo CVD process uses Hg vapours excited by exposure to UV(2537Å) radiation which catalyses the deposition of various nitrous oxide N<sub>2</sub>O. The oxygen and silane react to produce SiO<sub>2</sub> in addition to several by products including water. The electrical properties of the SiO<sub>2</sub>-HgCdTe interface are very sensitive to the presence of native oxides and photo chemical oxides prior to the SiO<sub>2</sub> deposition. Best results are obtained when a few layers of native oxide are present on HgCdTe before deposition. The oxide is so thin that it is either removed or incorporated into the SiO<sub>2</sub> during the deposition process. The interfaces are characterised with fixed surface charges that are low between scattered values ( $-1 \times 10^{10}\text{cm}^{-2}$ ) that imposes flat band condition and positive fixed charges as high as  $1 \times 10^{10}\text{cm}^{-2}$ . Interface trap density is as high as  $5 \times 10^{11}\text{cm}^{-2}$  and increases to  $5 \times 10^{11}\text{cm}^{-2}$  at the band edges. Slow traps are also revealed by hysteresis in the measured CV characteristics. The electrical properties of the interface are strongly affected by absorbed water which penetrates through the porous SiO<sub>2</sub> to

the interface. SiO<sub>2</sub> has excellent insulating characteristics with an energy gap  $E_g = 8\text{eV}$  It has a bulk resistivity ( $\rho$ ) 1013 ohm-cm The dielectric constant has a low value of  $\epsilon = 2.1$  due to the porous properties of the LT-CVD SiO<sub>2</sub>. Its index of refraction  $n = 1.5$  and depends on deposition rate and chamber pressure. SiO<sub>2</sub> is protective, but more porous and structurally different than the thermally grown SiO<sub>2</sub> on Si. It is affected by water that is either incorporated into the SiO<sub>2</sub> as SiOH during deposition or absorbed from the atmosphere and retained in the pores. Silicon dioxide films on MCT exhibit adhesion problems which are probably due to the different coefficients of thermal expansion of HgCdTe ( $5 \times 10^{-6}\text{K}^{-1}$ ) and SiO<sub>2</sub> ( $0.5 \times 10^{-6}\text{K}^{-1}$ ). The mechanical properties are also directly affected by the adhesion and are excellent when adhesion is adequate. The thermal stability is also adequate upto 90°C. Silicon dioxide is transparent in the 3-5  $\mu$ m spectral region. In the case of photo diode for detection of radiation in the 8-12  $\mu$ m region, SiO<sub>2</sub> can be used only for passivating rear side of illuminated devices.

### Silicon Nitride (15, 21):

The electron cyclotron resonance plasma chemical vapour deposition (ECR-PCVD) is another low temperature process for deposition of SiN<sub>x</sub>, on a HgCdTe substrate which is held at room temperature. In an ECR plasma CVD apparatus N<sub>2</sub> gas is introduced into a plasma chamber and is excited to a plasma state by ECR at a microwave frequency of 2.45 GHz, magnetic flux of  $8.75 \times 10^{-2}\text{T}$ . The N<sub>2</sub> plasma, effectively ionised by ECR falls into the reaction chamber where it enhances the reaction between silane (SiH<sub>4</sub>) and nitrogen. A dense SiN<sub>x</sub>, film is deposited at a temperature less than 95°C. The SiN<sub>x</sub>, film is seen to have a uniform composition with  $\text{Si} / \text{N} = 0.9$  over its depth and gives very good insulation. The MCT/SiN<sub>x</sub>, interfaces are characterised with low fixed charges of  $-1.4 \times 10^{11}\text{cm}^{-2}$  as well as low interface density of  $10^{11}\text{cm}^{-2}\text{eV}$  and carrier concentrations  $(0.5-1) \times 10^{16}\text{cm}^{-3}$ . Thus, the structure of P-type MCT is slightly accumulated at zero bias. In ECR-PCVD method of deposition of passivating film the MCT surface is damaged due to the striking of ions. The passivating layer of SiN<sub>x</sub>, film is very dense No conclusive data is available about the dielectric properties of SiN<sub>x</sub>. ECR plasma-CVD can be used for passivating MCT photodiodes. The SiN<sub>x</sub>, passivating film stabilises the diode in humid conditions When growing foreign layer of SiN<sub>x</sub>, on the surface of MCT one problem is the creation of electrically-active defects at the interface due to Hg being freed by the impact of deposition.

### Anodic Oxides (22-32):

The anodic oxides of MCT are its native oxides and are grown by the electrochemical process of anodisation which was earlier successfully employed in silicon and gallium arsenide technologies and later used for MCT in 1976 This process is carried out at room temperature in a solution of 0.1M KOH in 90% ethylene glycol/10%water The HgCdTe substrate is biased to positive polarity (anode) and carbon or platinum counter electrode is the cathode (negative polarity) anodization current density is of the order of 0.1 to 0.3 mA/cm<sup>2</sup> and voltage rises to -7-10V in 3-5 min. The fixed oxide surface charges at the interface are high, of the order of  $5 \times 10^{11}\text{cm}^{-2}\text{eV}^{-1}$  at centre of the gap The interface of n-type material are strongly accumulated while those of p-type are highly inverted. The fixed charges and surface conductivity

increases significantly above 75°C, lowering the resistance of photoconductor. Its insulating properties are adequate but inferior to SiO<sub>2</sub>, adhesion is excellent for thickness less than 1000Å but the native oxide is easily attacked by acids. The anodic oxides have direct effect on the composition and structure of the semiconductor surface because the fixed oxide charge can be reduced in Hg<sub>0.7</sub>Cd<sub>0.3</sub>Te if the semiconductor surface is subjected to electroetch prior to anodisation. But the same process has little effect on fixed charges for the MCT alloy with a higher fraction of mercury content, i.e., Hg<sub>0.8</sub>Cd<sub>0.2</sub>Te. The oxide grown by the anodisation process is amorphous and consisting of CdTeO<sub>3</sub>, and HgTeO<sub>3</sub>. The oxidation reaction anodization process is strong enough and damages the MCT surface HgCdTe to a depth of 200Å under the oxide interface. The stability of anodic oxide is a matter of concern because of the reactivity of its constituents with the MCT surface e.g. HgTeO<sub>3</sub> reacts with HgTe to form TeO<sub>2</sub>, and free mercury. Free mercury at interface could provide a conduction path resulting in leakage current and also diffuses into the semiconductor resulting in an n layer. The native oxides can be used for the surface passivation of n-type material for fabricating PC/MIS devices. Because of their large fixed positive charges they invert the surface of p-type MCT. This proves to be inadequate for the passivation of PV devices which are fabricated on p-type MCT.

#### Photochemical Oxides (33-39):

Native oxide of MCT is also grown by photochemical oxidation technique. The photochemical oxidation is carried out in a photochemical oxidation chamber which utilizes a low pressure mercury lamp with a sapphire window as the UV light source. The lamp has an output of 1mW/cm<sup>2</sup> at 1849Å and is therefore capable of significant oxygen atom production by photodissociation of N<sub>2</sub>O into N<sub>2</sub> and O<sup>1</sup>(D). Native photochemical oxide is grown by illuminating flowing N<sub>2</sub>O [flow rate=10std.cm<sup>3</sup>/min (scm), pressure =3.5Torr] with the HgCdTe substrate held in the temperature range from 40-100°C. Photochemical HgO is deposited with the same conditions as those for native oxide growth with addition of a Hg sensitizer by passing N<sub>2</sub>O over a pool of Hg. Photochemical growth mechanism includes both cation out diffusion and oxygen in diffusion, similar to that reported for anodic oxide growth. The HgCdTe photochemical native oxide interface properties are obtained with low fixed oxide charge density ~1.0x10<sup>11</sup>cm<sup>-2</sup> and low density of fast and slow interface traps. The interface properties are insensitive to the surface pre-treatment. The encapsulation of photochemical native oxide with photochemical SiO<sub>2</sub> degrades the interface properties. The presence of photochemical HgO between the native oxidend SiO<sub>2</sub>, results in superior HgCdTe surface electronic properties with low fixed charges 10<sup>10</sup> cm<sup>-2</sup>. But the MOS structure composed of SiO<sub>2</sub> on HgO with photochemical native oxide undergoes an electrical degradation at room temperature.

#### Plasma Oxides (37-39):

Plasma anodisation is another process for growing native oxides on semiconductors. Oxidation is accomplished here by using activated oxygen, created by an electrical discharge, as the oxidising species. This is usually carried out in a low pressure system (0.1-0.5torr). The advantage of plasma anodisation lies in the fact that the temperature of the

electrons of the ionised gas is about 10,000K as a result of which oxidation can be carried out at low thermal temperatures (<100°C). Plasma anodisation is carried out in a commercially available r.f. plasma stripper system. The oxygen plasma created by using r.f. source (power 20 - 200W) at 13.5 MHz has a thermal temperature of less than 50°C. The best interface properties have been achieved at low plasma power (30W) and moderate bias voltage (40-90V) which avoided the heating of sample and reduced the surface damage due to electron ion bombardment. The average growth rates were 20-30Å/min, the fixed surface charge density at interface is lower than anodic oxide and is ~ 1x10<sup>11</sup> cm<sup>-2</sup>. The dielectric properties of the plasma oxide are, however, inferior to those of the anodic oxide, since the former is less dense, has a lower dielectric constant and lower dielectric strength.

#### Anodic Sulphides (40-44):

A new process has been developed for the formation of native sulphide insulating films on MCT. The surface passivation is based on sulphide insulating films (usually CdS), which are grown by a process called anodic sulphidation. Native sulphide films of 200-400Å thickness are grown on MCT in a non-aqueous basic solution of Na<sub>2</sub>S at constant current densities of 50-100µA/cm<sup>2</sup>. The resulting CdS is further capped with a ZnS film of 1.0µm thickness. A fixed negative charge density of -5x10<sup>10</sup> cm<sup>-2</sup> and a fast interface state density of 1x10<sup>10</sup>cm<sup>-2</sup> eV<sup>-1</sup> have been achieved by this technique. The CdS films on MCT are stable upto 95°C though their adhesion is not so good for thickness greater than 1000Å. The dielectric properties of native sulphides are inferior to SiO<sub>2</sub> and they are easily attacked the growth by HCL. The combination of CdS and ZnS as passivating and insulating layers seem to be appropriate for PV devices. However, due to their complex nature mechanism of anodic sulphides needs more investigations to understand the combination of chemicals used for device processing.

#### Anodic Fluorides (44):

Anodic fluoride films are grown in an electrochemical cell onto a wafer of HgCdTe using a carbon counter electrode. Here anodization is a wet process performed both in aqueous and non-aqueous solution of KF or KF + KOH in ethylene glycol. The anodization current is constant and of the order of 0.1 to 0.3 mA/cm<sup>2</sup> and uses voltage upto 3-4V in 5-7 min. The growth mechanism can be understood in terms of the dissolution-precipitation model, which is similar to the anodic oxide growth mechanism. The anodic fluoride is composed of cadmium fluoride in a matrix of Te, Cd and Hg. It is free of oxygen when grown from non-aqueous solutions. In aqueous solutions one gets anodic oxide in addition to the anodic fluoride. Even a low hydroxyl ion concentration causes the growth of anodic oxide. The interfaces characterised by MIS devices composed of the anodic films and deposited ZnS films grown from a fluoride bath produce interface with a low fixed positive charge density ~2x10<sup>10</sup> cm<sup>-2</sup> for n-type, and ~5x10<sup>10</sup> cm<sup>-2</sup> for p-type materials. Anodization with high current densities (400µA/cm<sup>2</sup>) results in a lower fixed positive charge densities. The electrical behaviour of anodic films grown from a KF + KOH mixture is different from that of anodic films grown from fluoride free bath. The band bending at the semiconductor surface can be controlled by choosing the appropriate ratio of OH and F ions

in anodization path. Interface passivation with anodic fluoride films grown with relatively high current densities ( $400 \text{ Acm}^{-2}$ ) are stable upto  $105^\circ\text{C}$ . In case of  $\text{KF} + \text{KOH}$  solutions, higher  $\text{OH}^-$  concentration results in greater increase in the fixed charge density after annealing above  $70^\circ\text{C}$ . The insulating properties of anodic fluorides are adequate but inferior to  $\text{SiO}_2$  and  $\text{ZnS}$ . They are not very durable chemically and easily attacked by acid. The adhesion, chemical composition and dielectric properties of these films are undetermined.

### 3. Discussions

The variable band gap  $\text{HgCdTe}$  (MCT) is a very promising material, because of its utility in the fabrication of IR detectors (45), solar cells, optical wave guides (46), microwave oscillators, amplifiers and mixers. It is a very popular material, particularly at the composition range  $x = 0.2$ , which corresponds to a band gap of  $0.1 \text{ eV}$ , ideal for the IR region. In spite of being suitable in all respects for use in the IR region,  $\text{HgCdTe}$  (MCT) suffers from one drawback, of being unstable. This leads to surface defects, surface recombination, dangling bonds, etc., which degrade device performance. One solution to this problem is to passivate the surface of  $\text{HgCdTe}$  (MCT). Some research has been carried out in this direction. There are many factors that govern the choice of a suitable passivant, like stability, adherence, non-porosity, resistance to chemicals necessary for the fabrication process, good insulator properties, low interface state density, low insulator oxide fixed charge density, etc. The choice of a passivant material and technique is particularly difficult in the case of in  $\text{HgCdTe}$  (MCT) of the complex chemistry and temperature sensitivity of this material. A large number of materials and deposition techniques have been employed for the passivation. However, the passivation technology is not yet well established. Low Temperature-CVD,  $\text{SiO}_2$  in combination with native oxides (16, 18), deposited  $\text{ZnS}$  (9-13) and  $\text{SiN}_x$ , (14-21) as well as native oxide sulphide in combination with thermally evaporated  $\text{ZnS}$  are commonly applied to passivate MCT photodiodes (47-48), Evaporated  $\text{ZnS}$  and  $\text{SiO}_x$  deposited by photo CVD at low temperature also provide passivation layers for PV devices but they cannot be considered as ideal passivants. When placing foreign layers of  $\text{ZnS}$  and  $\text{SiO}_2$  on the surface of  $\text{HgCdTe}$  (MCT), one problem is the creation of electrically active defects at the interface due to Hg being fixed by the 'impact' deposition. If  $\text{HgCdTe}$  (MCT) is raised to elevated temperatures" in order for deposition to take place as for  $\text{SiO}_2$ , there can be the additional problem of Hg out diffusion from the  $\text{HgCdTe}$  (MCT). With  $\text{SiO}_2$ , the problem is reduced by reducing deposition temperature down to  $80^\circ\text{C}$  and by using photo excitation. The instability of  $\text{ZnS}$  to temperature cycling is probably associated with lack of deposition at elevated temperature. So, the  $\text{ZnS}$  layer offers instability to temperature cycling, is not a very good insulator, attacked by air and  $\text{H}_2\text{O}$  soluble (9-13) Also fixed charges are produced when it is exposed to blue or ultraviolet light. The LT-CVD grown  $\text{SiO}_2$ , though an excellent insulator, has its own drawbacks; it offers adherence problems, is porous, absorbs moisture and is contaminated by atmospheric gases. It is known that there is great difference in chemical activities of the three constituents of MCT Hg, Cd, Te and in the stability of their oxides. The anodic oxides as passivant layers have charge defects near the  $\text{HgCdTe}$  /oxide interface. These may

be due to the difference in activity of Hg, Cd, Te. It is not possible to grow anodic oxide without creating such defects. Even if this were achieved, the chemical interaction between the passivant and  $\text{HgCdTe}$  (MCT) would be a problem. Though various materials have been tried out for passivation of MCT surface like  $\text{ZnS}$  (31-35)  $\text{SiO}_2$  (36-42),  $\text{SiN}_x$ , (36,43) and native oxides (44-53) etc. but all these suffer from one drawback or the other. After taking into account all the problems posed by various passivants reviewed in literature then it is decided to try a new passivant material, viz.  $\text{CdTe}$ , which is expected to be better than all the materials tried so far. Thus, for this project, the new versatile material  $\text{CdTe}$  has been tried out to passivate MCT by physical vapour deposition techniques in order to produce superior and more consistent interface. It is chosen because of its certain advantages in material properties.

- 1)  $\text{CdTe}$ , being the native material of the  $\text{HgCdTe}$  alloy system, can naturally give good interface properties with the  $\text{HgCdTe}$  (MCT) surface due to its small lattice mismatch of 0.2% percent. (Lattice constant of  $\text{HgCdTe} = 6.463 \text{ \AA}$  and lattice constant of  $\text{CdTe} = 6.477 \text{ \AA}$ .) (51)
- 2) Both  $\text{CdTe}$  and  $\text{HgCdTe}$  have the same zincblende structure.
- 3) The linear thermal expansion coefficients (49,50) of MCT and  $\text{CdTe}$  at  $25^\circ\text{C}$  are at  $5.5$  and  $4.3 \times 10^{-6} \text{ }^\circ\text{K}^{-1}$ , respectively. The ratio of the two coefficients comes around 88% and suggests very good adhesion of  $\text{CdTe}$  to  $\text{HgCdTe}$
- 4) Being a higher band gap material with  $E_g = 1.6 \text{ eV}$ ,  $\text{CdTe}$  is optically transparent to IR radiation and provides electrical and chemical stability to the  $\text{HgCdTe}$  surface
- 5) It is mechanically harder than  $\text{HgCdTe}$  (MCT) and non-hygroscopic.

### 4. Conclusions

$\text{HgCdTe}$  remains a highly important material for infrared detection, but its unstable surface chemistry makes effective passivation essential. Existing passivation approaches, including  $\text{ZnS}$ ,  $\text{SiO}_2$ ,  $\text{SiN}_x$ , and native oxide-based systems, provide useful protection, but each has notable limitations in stability, interface quality, or environmental durability. Based on material compatibility considerations,  $\text{CdTe}$  appears to be a promising candidate for future passivation studies. However, further experimental validation is required to establish its superiority over existing approaches.

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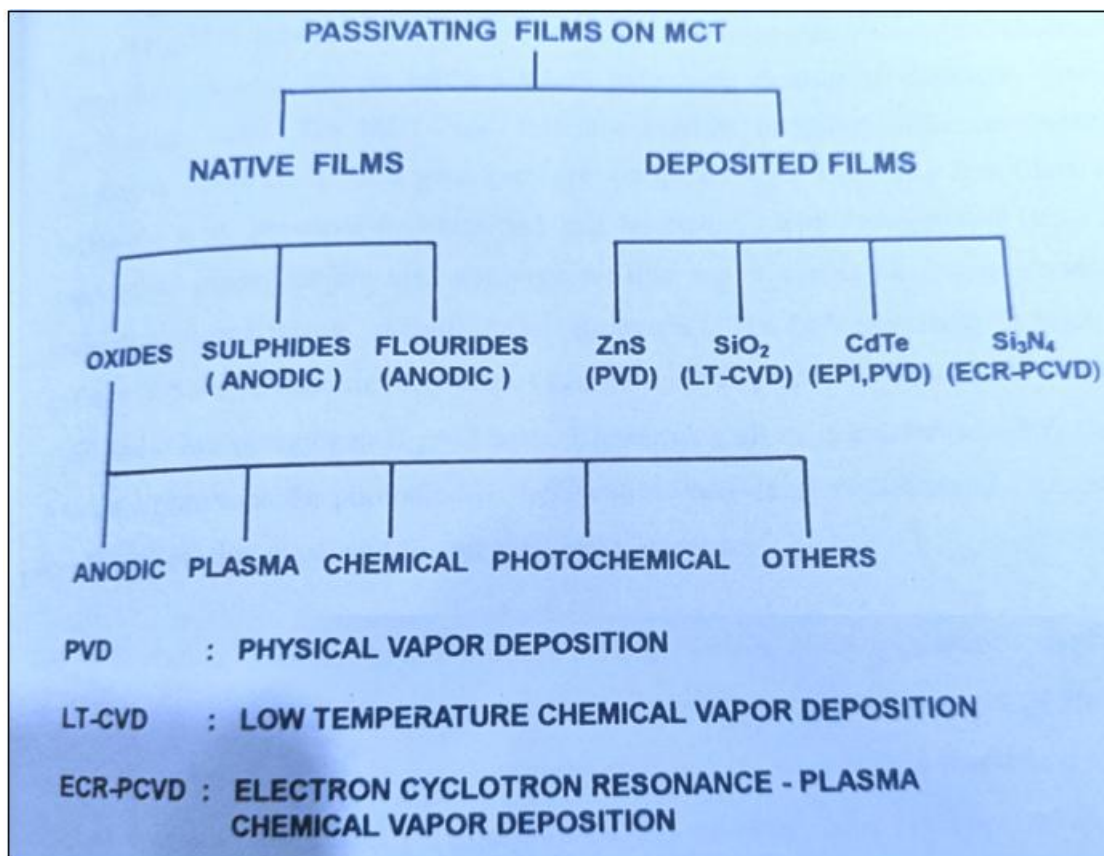


Figure 1: Different Passivating Films on HgCdTe