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State of the art of the heavy metal iodides as photoconductors for digital imaging

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ABSTRACT

The current status of the development of the heavy metal iodides as photoconductors for direct and digital imaging is reviewed. The physical properties of these materials are first summarized as regards their application as photoconductors and the growth of their layers onto readout matrixes for digital imaging. A comparison of the results obtained for polycrystalline and oriented layers of mercuric iodide, lead iodide and bismuth tri-iodide, grown by Physical Vapor Deposition (PVD), is presented. The three materials were found to have similar behavior; the influence of layers orientation on electrical properties and on response to radiation is also evaluated. The best results (DQE, MTF, and actual images) reported for devices made with mercuric and lead iodide layers grown onto TFT and CMOS are remarked, and device performance is compared with the one of alternative materials such as a-Se and CdTe. Perspectives of the field such as using nanostructures as precursors for growing epitaxial layers, and possible future research, are also presented.

1. Introduction

Over the past 15 years, the production technology of active matrix, flat-panel imagers such as thin film transistors (TFT) and complementary metal–oxide–semiconductors (CMOS), has developed considerably, and so has the procedure for further image processing. This has brought about the introduction of a new generation of digital ionizing radiation imaging devices that are based on the growth of layers of materials appropriate for radiation detection onto such imagers. They have medical, industrial, security, scientific and cargo inspection applications. Among medical applications, static mammography and radiography, real time and portal imaging are some of the fields where these devices can bring considerable improvement.

Advantage can be taken of active matrix technologies, first, by producing indirect imaging devices, depositing a scintillator onto them, which will collect the light produced by the radiation, or second, by the direct method, growing layers of appropriate semiconductors onto the array. In these last devices, each pixel of the array will be a rear contact, which will give the signal for the corresponding pixel in the final image. A metallic layer, deposited onto the semiconductor, acts as the front contact. When radiation is absorbed, electron–hole pairs are produced in the semiconductor, and the applied field directs them towards the electrodes; in this way, each radiation produces a much less dispersed signal [1,2]. In addition to the benefits because of being both digital, several advantages may be expected, for the direct over the indirect method of imaging, such as a better modulation transfer function (MTF), a higher detective quantum efficiency (DQE), and a lower image lag [3].

When the intention is to grow layers for direct and digital imaging, the application determines the substrate, the layer material, the detection process, required properties of the layers and even the features of the growth method.

The final substrate will be a TFT or a CMOS, which are non-uniform and amorphous, and which will be—only thinking in medical applications—from $2\times2\,\mathrm{cm}^2$ to about $40\times40\,\mathrm{cm}^2$ in area. For preserving the stability of these devices when used as substrates for growing semiconductor layers onto them, the growth process will be restricted to temperatures up to 200 °C and time up to 1 day. As the active matrix field is in continuous development, large area matrixes, especially designed for imaging, and other technologies such as nano-CMOS will have to be taken in mind when designing the final radiation imaging device.

The layer material, core of the device, should be a semiconductor with suitable properties such as high atomic absorption coefficient, wide energy band gap (E_g) but low mean energy transferred by the incident radiation during the process of generation of an electron–hole pair (ε), and high mobility-life-time product ($\mu\tau$) for electrons and holes. Furthermore, a high purity and a good stoichiometry have to be achieved for such a material. A variety of materials such as a-Si [4,5], a-Se [3,6–10], TlBr [11–13], CdTe [14–21], CZT [22,23], PbO

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[24–26], $HgBr_2$ and $PbBr_2$ [27–29], HgBrI [30], HgI_2 [31–59], PbI_2 [60–70] and BiI_3 [71–74] have been studied as photoconductors for digital radiation imaging. Among these materials, the heavy metal iodides have turned out to have properties that are especially suitable for the purpose. From the point of view of radiation detectors, they have elements with high atomic number, and high density, which determine a lower thickness (70–165 μm is enough for 99% of absorption of 20 keV radiation). They have wide energy band gap (BiI_3: 1.7 eV, HgI_2: 2.1 eV, PbI_2: 2.5 eV, at room temperature) therefore they may give a lower dark current through the detector without any cooling [75,76]. On the other hand, they do not follow [78,79] Klein's relation [77] and therein they have a relatively low ε (4–5 eV) and may give a higher signal to noise response. As a major drawback, these materials give ($\mu\tau$) products for electrons and holes (10^{-4}–10^{-7} cm^2/V) lower than the ones of the alternative materials [76]. From the point of view of the growth of layers, although the heavy metal iodides have similar properties, mercuric iodide is quite different from lead iodide and bismuth tri-iodide, maintaining these two important similarities. For instance, at normal conditions, mercuric iodide exists in its tetragonal red α phase, and has a phase transformation at 127–131 °C at normal pressure, from α-HgI_2 to β-HgI_2 (orthorhombic and yellow) [80]. Among others, there also exists another yellow phase of mercuric iodide [81], and an orange phase [82,83], with three polytypes [84], all of them unstable at room temperature. There are no reports about any tendency of mercuric iodide to decompose. Meanwhile, lead iodide and bismuth tri-iodide do not have phase transformations–lead iodide presents several polytypes [85,86], but have the tendency to dissociate in the vapor phase, stronger in the lead iodide case [87]. Mercuric iodide has a low melting point (256 °C) and a high vapor pressure even below it [80]. Instead, lead iodide and bismuth tri-iodide have melting points in the order of 402–408 °C and an appreciable vapor pressure below their melting points [88], although lower than that of mercuric iodide.

It is important to remark the extremely high reactivity of mercuric iodide with most of the chemical substances [89], especially some metals such as aluminum or gold. Some exceptions such as glass, quartz, stainless steel, and–partially–palladium [90] permit to construct systems for growing their layers, or to select metals to be used as electrodes when assembling detectors with it. Lead and bismuth iodide are substantially less reactive, although BiI_3 clearly reduces stainless steel. On the other hand, all of them are toxic, with mercuric iodide with the highest toxicity [91].

The heavy metal iodides are layered compounds, whose crystal lattices are built from three layer packages (I–Hg–I; I–Pb–I; I–Bi–I) with weak van der Waals bonding between adjacent planes of iodine atoms and perpendicular to the c axis [92–94]. This layered structure determines a high anisotropy for most of the properties of these compounds, such as a difficult cleavage along the *c* axis but an easy one perpendicular to it, and different values of thermal conductivity and expansion coefficients along the different axis [95,96], which have to be considered for layer growth.

The detection process will involve radiation absorption, the generation and transport through the semiconductor of charge carriers, and their collection at the electrodes. Maximum radiation absorption will take place when the layers of crystalline planes are oriented parallel to the substrate, that is to say perpendicular to the radiation beam. Better charge transport will occur through an oriented layer, or, even better still, through an epitaxial layer. The best charge collection will take place for plain front electrodes, such as those which may be deposited on the surface of an epitaxial layer. Also, the dark current through the layer (thermally generated or injected from electrodes) should not exceed 1000 pA cm^{-2} for proper working of TFT or CMOS [3].

It is clear from the paragraph above that the detection process imposes the required properties of the layers, and therein, the main challenge in developing ionizing radiation digital imaging sensors is to grow adequate semiconductor epitaxial layers onto amorphous substrates such as TFTs or CMOs, with areas up to about 40×40 cm^2 for medical application, thicknesses of about 100–200 μm, and with the appropriate orientation. These layers should give the maximum sensitivity, the best spatial resolution, and a quick response. Last but not least, the final application demands uniformity of properties for the complete layers active area.

The previous specifications determine the features of the growth method of these semiconductor layers. For growing them, it is necessary to select a method whereby the material does not decompose (stoichiometry), the growth temperature is below 200 °C and the growth time less than 1–2 days, and layers thickness, orientation, crystal quality and uniformity are suitable. The process must also be easy to scale-up to large areas, and production cost must be competitive. There is a considerable experience in growing semiconductors epitaxial layers from a few nanometers to a few micrometers in width for a wide range of applications. There is also reported work on oriented crystallization on amorphous substrates [97]. However, the artificial epitaxial growth of layers about 100–200 μm in thickness and large in area has not yet been requested for other technological applications. Therefore, the challenge of growing epitaxial layers of heavy metal iodides onto amorphous substrates, suitable for digital radiation imaging, remains unsolved.

Once summarized the main issues related to the heavy metal iodides as photoconductors for digital imaging, in the following sections the experimental techniques involved in such field, as far as a comprehensive view of the current status of its development are presented.

2. Main experimental techniques employed in the field

A vast number of experimental techniques have been used for the preparation and characterization of heavy metal iodide direct imagers.

High purity chemicals have been used as starting materials; zone refining has been the purification method for mercuric iodide; zone refining, followed by repeated sublimation, showed to be a particularly suitable procedure for purifying and, at the same time, restoring stoichiometry in the lead iodide and bismuth tri-iodide cases [87,98]. Whereas the purity of the starting material was several times correlated with the spectrometry performance of the detectors made with crystals of these iodides, this is not the case for the imagers made from the layers, in which purity was only occasionally mentioned [66].

Although the final performance of the layers must be checked by growing them on an active matrix, and sometimes it was, several studies were done using sample detectors which consist of the heavy metal iodide, theoretically of the same quality and thickness as will be used on the final array, deposited between electrodes on simpler substrates such as alumina and glass, coated with metals (Palladium and Gold) or ITO. Layers have been grown onto TFTs [41,45,50,60,63,64,99,100, and 109] and CMOS [46,54]. The high reactivity of mercuric iodide leads to foresee its reaction with metals of TFT and CMOS circuitry; this reaction was avoided by using a conductive polymer blocking layer between layer and array [57,58,101].

Several methods have been used for growing layers of heavy metal iodides such as laser ablation, screen print [33,34], electrodeposition, growth from solution [42] and from the vapor phase. Due to the high vapor pressure of these compounds below their melting points the physical vapor deposition method (PVD) was mainly adopted as suitable for growing layers of usable size at practical growth rates. As there are no commercial equipment