Colloidal Quantum Dot Image Sensor Technology

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Abstract

Colloidal quantum dot (CQD) technology is now being used commercially for its ability to absorb a broad spectrum of wavelengths of light and convert that light into photocurrent. After roughly 20 years of R&D, CQD-based image sensors are the first commercial products in the marketplace to use CQDs in electro-active devices in contrast to all the other current products that use CQDs in photoluminescence mode. The CQD sensor industry is now focused on the short-wave infrared (SWIR) region of the spectrum because of silicon's inability to sense in this range and due to a strong value-proposition for CQD image sensors versus other technologies in the SWIR imaging space such as InGaAs and SiGe.

We have scaled up this new platform technology to our 300mm manufacturing toolset. The challenges associated with the introduction of solution-processed, colloidally grown lead sulfide (PbS) QDs in an industrial 300mm fab environment were successfully overcome. The robustness of our 300mm Quantum Film technology was fully assessed and reliability in terms of meeting all required lifetime specifications for consumer electronics and other potential applications has been demonstrated. Pixel architecture versatility combined with low-cost and broad spectral sensing capabilities create a great opportunity to use CQD image sensors for a diverse set of sensing needs in the industry now and into the future.

INTRODUCTION

Short-wave infrared (SWIR) image sensing has remained for decades a niche technology market dominated by very high-cost InGaAs sensor array technology. Very recently, however, colloidal quantum dot (CQD) photodetector technology has emerged as a commercial technology able to challenge InGaAs and SiGe semiconductor image sensor technologies traditionally used to address wavelengths in the SWIR region of the light spectrum from 1000nm to 2500nm [1,2]. The tremendous potential of CQD image sensor technology to revolutionize the SWIR imaging market is stimulating the InGaAs and SiGe image sensor industry to respond aggressively by cutting costs, improving performance, and expanding markets [3,4].

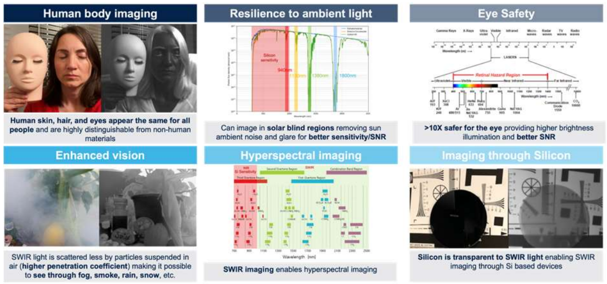
The potential of CQD image sensor technology to expand SWIR image sensing into the consumer market is based on our ability to now manufacture it on 300mm CMOS wafers and provide it to the industry at the required volumes and costs [5,6]. This is possible because the technology uses thin films of chemically synthesized semiconductor nanoparticles (quantum dots), called Quantum Film, to absorb a large amount of light, due to quantum confinement, to create high-performance and low-cost sensor arrays capable of sensing from the UV to the extended SWIR portion of the spectrum [7,8]. The large spectral response is tunable and capable of being optimized at specific regions of the spectrum based on the CQD particle size used to make the Quantum Film [9,10]. The large absorption cross-section of Quantum Film enables the creation of thin absorbing layers in the device stack to reduce pixel crosstalk and give improved resolution down to 1.62um and 2.2um pixel pitch global shutter image sensors with high quantum efficiencies at the first excitonic peak of greater than 60% [6].

The PbS CQD photodetector device stacks are integrated above IC on 300mm CMOS wafers with a 100% fill-factor enabling the shrinking of complex global shutter pixel architectures. This combined with the relatively low cost of the colloidally synthesized QDs and spin-coated layers on 300mm CMOS wafers allows ST to make CQD image sensors at a cost similar to Si-based image sensors [6].

SWIR IMAGING FOR THE CONSUMER MARKET

The strongest value proposition in the market for new sensor technologies is created by targeting applications that Si technology cannot address. Si absorption cuts off around 1000nm, so low-cost, high-performance imaging in the SWIR has become the area of interest [6,9]. The most established markets in SWIR imaging are dominated by defense and machine vision and are niche image sensor markets where cost is not a driver. For the industry to use SWIR image sensing in the high-volume consumer and automotive markets, it needs to enable new features and user experiences that are not possible using the visible and 940nm wavelengths of light that Si sensors can address.

The exploration to find applications where the use of SWIR wavelengths can create large value versus sensing in the visible and 940nm regions of the spectrum is currently underway in the industry and was started because of the recent emergence of low-cost CQD SWIR image sensor technology [9]. SWIR imaging in consumer and automotive markets could enable a whole set of new features and user experiences based on several unique advantages of sensing beyond 1000nm as summarized in Figure 1.



Human body imaging

Human skin, hair, and eyes appear the same for all people and are highly distinguishable from non-human materials

Resilience to ambient light

Can image in **solar blind regions** removing sun ambient noise and glare for **better sensitivity/SNR**

Eye Safety

>10X safer for the eye providing higher brightness illumination and **better SNR**

Enhanced vision

SWIR light is scattered less by particles suspended in air (**higher penetration coefficient**) making it possible to **see through fog, smoke, rain, snow**, etc.

Hyperspectral imaging

SWIR imaging enables hyperspectral imaging

Imaging through Silicon

Silicon is transparent to SWIR light enabling SWIR imaging through Si based devices

Fig. 1. Summary of many SWIR imaging advantages versus visible and 940nm light sensing.

Human skin, hair, and eyes all appear the same in the SWIR for all people of different skin color, eye color, and hair color. Ambient light is significantly reduced when imaging in the solar blind regions of the spectrum at 1130nm, 1380nm, or 1800nm, removing ambient noise and glare for better sensitivity and signal-to noise. SWIR light is greater than 10 times more retina safe versus 940nm light, permitting safer active imaging illumination applications and better signal-to-noise. SWIR light is strongly absorbed by water allowing very good contrast for anything containing some amount of water. Many materials such as plastics and silicon are transparent to SWIR light enabling high-contrast imaging through plastics and through Si-based devices. The first, second, and third overtone regions of most organic molecules fall into the region of the SWIR spectrum enabling the fabrication of low-cost, high-performance, hyperspectral imaging and mini spectrometers. SWIR light is scattered less by particles suspended in air making it possible to see through foggy glass, smoke, snow, rain, dust, and fog. With so many unique advantages, for the first time available at low-cost, high-volume, and high-performance, it will be exciting to see how SWIR imaging technology penetrates the consumer and automotive markets in the coming years.

FABRICATION OF SWIR IMAGE SENSORS ON 300MM WAFERS

The successful introduction of colloidally grown and solution deposited PbS semiconductor nanoparticles (CQDs) into an industrial 300mm Si wafer fab environment was a huge undertaking and an exciting achievement [5,6]. Bringing together traditional semiconductor manufacturing on 300mm wafers with solution processed semiconductor technology was a world's first and has set the stage for continued innovation along these lines worldwide.

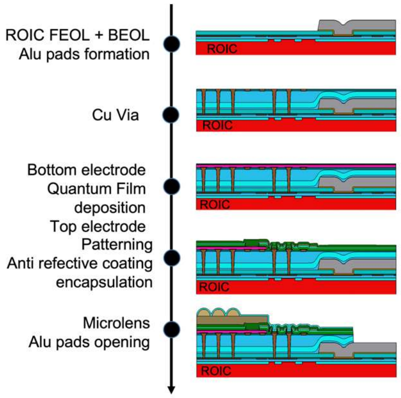


Fig. 2. CQD sensor fabrication process flow.

The CQD photodiode array is monolithically integrated on top of an ROIC circuit fabricated using a custom imager CMOS front side technology [6]. This process flow is shown in Figure 2. The PbS CQD device stack is fabricated by spin coating layers of colloidally grown PbS CQDs on top of the ROIC circuit as shown in Figure 3, including a cross section of the CQD photodiode. The CQD formulation and the spin-coating process were optimized for low film stress, high film uniformity and low number of defects. The CQD formulation was highly engineered to enable good colloidal stability over long periods of time in large volumes of solution for shipping, storing, and on-tool usage.

A qualification mask set was designed that included elementary CQD photodiode test structures, pixel array test chips, and full image sensor products [6]. A 300mm CQD wafer fabricated with this mask set is shown in Figure 4 and was used to assess the robustness of our CQD technology [11]. Full characterization is performed at the wafer and package level at 60°C using different infrared light sources [6].

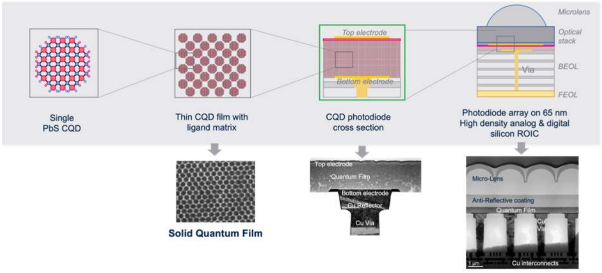


Fig. 3. CQD photodiode array integrated on top of CMOS readout IC, CQD photodiode cross section, and graphical depiction of the CQD device stack.

One of the many important aspects we had to address when handling PbS CQDs in an industrial 300mm fab environment was to prevent any metal cross contamination.

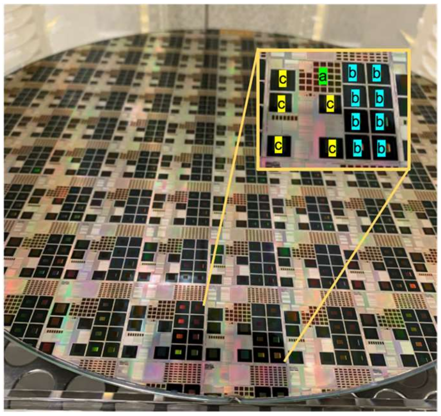


Fig. 4. CQD sensor technology qualification wafer showing elementary CQD photodiode test structures (a), pixel matrix test chips (b), and full image sensor products (c).

We use a dedicated lithography track system that was engineered specifically for CQD material coating. It is also integrated into an enclosure under constant nitrogen flow, with oxygen levels controlled down to a few ppm. A dedicated purged foup was also introduced to maintain an oxygen-free environment when wafers are moving from the lithography track to the top electrode deposition tool. This protocol is maintained until the CQD material is hermetically sealed by dielectric layers [6].

Another fundamental aspect we had to overcome when integrating CQD materials into a real process flow in the fab was to preserve its performance during the subsequent thermal treatments. CQD materials are more susceptible to degradation at high temperatures due to the weaker interaction of molecular ligands bound to the particle surface. As such, we developed lower temperature process flows to keep the CQD devices below 150°C for the fabrication of the top electrode, the encapsulation layers, and the micro lens array. Also, a lower temperature black resist process was developed to be compatible with the CQD pixel array, which is used to reduce the amount of light reflected off of the logic area surrounding the pixel array [6].

CONCLUSIONS

ST has scaled up our PbS colloidal quantum dot technology to a 300mm manufacturing toolset. The challenges associated with the introduction of solution-processed, colloidally grown lead sulfide QDs in an industrial 300mm fab environment were successfully overcome and was a world's first that has set the stage for continued innovation along these lines worldwide. The potential of CQD image sensor technology to expand SWIR image sensing into the consumer market is based on our ability to now manufacture it on 300mm CMOS wafers and provide it to the industry at the required volumes and costs. The exploration to find applications where the use of SWIR wavelengths can create large value versus sensing in the visible and 940nm regions of the spectrum is currently underway in the industry. SWIR imaging could enable a whole set of new features and user experiences based on several unique advantages of sensing beyond 1000nm. Pixel architecture versatility combined with low-cost and broad spectral sensing capabilities create a great opportunity to use CQD image sensors for a diverse set of sensing needs in the industry now and into the future.

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ACRONYMS

CQDs: Colloidal Quantum Dots
SWIR: Short-Wave Infrared (1000nm to 2500nm)
NIR: Near Infrared (800-1000nm)
ST: STMicroelectronics
PbS: Lead Sulfide
InGaAs: Indium Gallium Arsenide
SiGe: Silicon Germanium