

(51) International Patent Classification:  
*H01L 27/146* (2006.01)(21) International Application Number:  
PCT/US2014/032579(22) International Filing Date:  
1 April 2014 (01.04.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
61/807,058 1 April 2013 (01.04.2013) US  
14/198,175 5 March 2014 (05.03.2014) US(71) Applicant: **KLA-TENCOR CORPORATION** [US/US];  
KLA-Tencor Corporation, Legal Department, One Techno-  
logy Drive, Milpitas, California 95035 (US).(72) Inventors: **CHUANG, Yung-Ho Alex**; 10678 Farallone  
Drive, Cupertino, California 95014 (US). **BROWN, David L.**; 120 Wooded View Drive, Los Gatos, California 95032  
(US). **FIELDEN, John**; 2020 Victoria Court, Los Altos,  
California 94024 (US).(74) Agent: **MCANDREWS, Kevin**; KLA-tencor Corp., Legal  
Department, One Technology Drive, Milpitas, California  
95035 (US).(81) Designated States (unless otherwise indicated, for every  
kind of national protection available): AE, AG, AL, AM,  
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,  
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,  
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,  
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,  
KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME,  
MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,  
OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA,  
SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM,  
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM,  
ZW.(84) Designated States (unless otherwise indicated, for every  
kind of regional protection available): ARIPO (BW, GH,  
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ,  
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,  
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,  
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,  
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,  
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,  
KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

[Continued on next page]

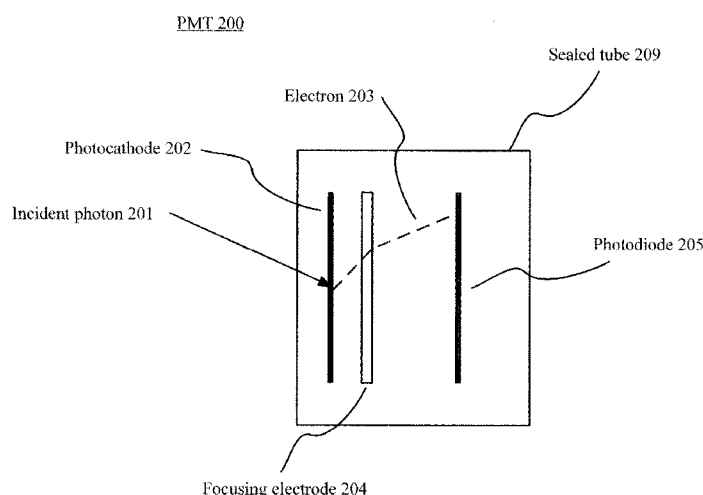
(54) Title: PHOTOMULTIPLIER TUBE, IMAGE SENSOR, AND AN INSPECTION SYSTEM USING A PMT OR IMAGE  
SENSOR

Figure 2

(57) Abstract: A photomultiplier tube in-  
cludes a semiconductor photocathode and a  
photodiode. Notably, the photodiode includes  
a p-doped semiconductor layer, an n-doped  
semiconductor layer formed on a first surface  
of the p-doped semiconductor layer to form a  
diode, and a pure boron layer formed on a  
second surface of the p-doped semiconductor  
layer. A gap between the semiconductor pho-  
tocathode and the photodiode may be less  
than about 1 mm or less than about 500  $\mu$ m.  
The semiconductor photocathode may in-  
clude gallium nitride, e.g. one or more p-  
doped gallium nitride layers. In other embod-  
iments, the semiconductor photocathode may  
include silicon. This semiconductor pho-  
tocathode can further include a pure boron  
coating on at least one surface.



- 
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

PHOTOMULTIPLIER TUBE, IMAGE SENSOR, AND AN INSPECTION SYSTEM  
USING A PMT OR IMAGE SENSOR

PRIORITY APPLICATION

[0001] This application claims priority to U.S. Provisional Patent Application 61/807,058, entitled "PMT, Image Sensor, and an Inspection System Using a PMT or Image Sensor", filed on April 1, 2013, and incorporated by reference herein.

RELATED APPLICATIONS

[0002] This application is related to U.S. Patent Application 13/710,315, entitled "Electron-bombarded charge-coupled device and inspection systems using EBCCD detectors", filed on December 10, 2012, U.S. Provisional Patent Application 61/658,758, entitled "Electron-bombarded CCD and inspection systems using electron-bombarded CCD detectors", filed on June 12, 2012, U.S. Patent Application 13/792,166, entitled "Back-illuminated sensor with boron layer", filed on March 10, 2013, and U.S. Patent Application 13/947,975, entitled "PHOTOCATHODE INCLUDING SILICON SUBSTRATE WITH BORON LAYER", filed on July 22, 2013. All of the above applications are incorporated by reference herein.

BACKGROUND OF THE DISCLOSURE

RELATED ART

[0003] Photomultiplier tubes (PMTs) and electron-bombarded charge-coupled devices (EBCCDs) using alkali metal photocathodes and infra-red sensitive III-V semiconductor (such as GaAs) photocathodes are known in the art for use at infra-red and visible wavelengths. Only alkali metal photocathodes have found widespread use for ultra-violet (UV) wavelengths.

[0004] Figure 1 illustrates a known PMT 100 including a photocathode 102, a focusing electrode 104, multiple dynodes 105 (three are shown for illustrative purposes, but a more typical number would be between five and twelve), and an anode 106. All of these components are contained in an evacuated sealed tube 109. The photocathode 102, the focusing electrode 104, the dynodes 105 and the anode 106 have electrical connections (not shown for simplicity). Each dynode 105 is held at a slightly positive voltage relative to the prior dynode 105 (or photocathode 102 for the first dynode). The anode 106 is held at a more positive voltage relative to the last dynode.

[0005] When an incident photon 101 is absorbed by the photocathode 102, there is a reasonably high probability (typically between about 10% and 50% in practical devices) of one or more electrons 103 being ejected from the photocathode 102. The focusing electrode 104 deflects the electrons 103 so that most of them will strike the first dynode. When an electron 103 strikes a dynode 105, it will usually cause multiple (typically about 10) secondary electrons to be ejected from that dynode 105. Figure 1 illustrates this ejection by showing more dashed lines leaving each dynode 105 than striking it. Most of the electrons ejected from one dynode strike the next dynode. This is repeated multiple times, until the amplified signal strikes the anode 106. Thus, the more dynodes 105 in a PMT, the greater the gain, but the longer the time taken for the device to respond to a single photon. Because some electrons from one dynode may miss the next dynode and strike another dynode or the anode 106, more dynodes 105 also mean a broader electrical pulse in response to a single photon, and hence a slower device.

[0006] Although Figure 1 illustrates a transmissive photocathode where the photoelectrons are ejected from the opposite side of the photocathode to the incident photons, reflective photocathodes are also known in the art, where the photoelectrons are ejected from the same side of the photocathode as the incident photons.

[0007] UV wavelengths of about 350 nm and shorter correspond to photon energies of about 3.5 eV and greater. When high energy photons are absorbed by the photocathode 102, electrons 103 with an energy of one, or several, eV are generated. Those electrons, after leaving the photocathode 102 and accelerated by an electric field, travel towards dynodes 105 and anode 106 (or an image sensor in an electron-bombarded image sensor). Because of a spread in magnitude and direction of their velocities due to their initial kinetic energy (e.g. one or more eV), the electrons 103 spread laterally as they travel towards the next surface. Moreover, these photoelectrons also arrive at different times at that surface.

[0008] In an image sensor, these different arrival times cause blurring of the image. In the PMT 100, these different arrival times slow the response time of the PMT because a single absorbed photon results in a pulse of current that is spread out in time due, at least in part, to the spread in arrival times of the electrons. A further disadvantage of the PMT 100 is that, in order to detect single photons, multiple stages of gain (dynodes 105) are required so that the signal from a single photon is greater than the background noise. Multiple dynodes further slow the response time of the PMT 100. Furthermore, detection of single photons with most conventional photocathodes requires a period of dark adaptation time after exposure to bright light

before dark current settles down to a low level. Some photocathodes require cooling to reduce the dark current to levels that allow reliable detection of single photons.

[0009] Therefore, a need arises for a photocathode with high quantum efficiency at UV wavelengths, while generating electrons with a low energy spread. A need also arises for a PMT incorporating this efficient, low-electron-energy-spread photocathode. A need also arises for a PMT with single-photon sensitivity, fast response and quick recovery to full sensitivity from high levels of light. A need also arises for an electron-bombarded image sensor, such as an electron bombarded charge coupled device (CCD) or an electron bombarded CMOS image sensor, that has high quantum efficiency, high spatial resolution and low noise. A need also arises for a dark-field wafer, photomask, or reticle inspection system using UV wavelengths and incorporating a high efficiency, low noise PMT, EBCCD, or electron-bombarded CMOS image sensor.

#### SUMMARY OF THE DISCLOSURE

[0010] A photomultiplier tube incorporating an efficient, low-electron-energy-spread photocathode is described. This photomultiplier tube includes a semiconductor photocathode and a photodiode. Notably, the photodiode includes a p-doped semiconductor layer, a n-doped semiconductor layer formed on a first surface of the p-doped semiconductor layer to form a diode, and a pure boron layer formed on a second surface of the p-doped semiconductor layer. A gap between the semiconductor photocathode and the photodiode may be less than about 1 mm or less than about 500  $\mu\text{m}$ .

[0011] In one embodiment, the semiconductor photocathode can include gallium nitride. For example, the semiconductor photocathode may include one or more p-doped gallium nitride layers. In another embodiment, the semiconductor photocathode can include silicon. Such a semiconductor photocathode can further include a pure boron coating on at least one surface.

[0012] A system for inspecting a sample is also described. This system includes a laser system for generating light. First components direct that light to the sample. Second components direct light from the sample to one or more detectors. At least one detector includes a photomultiplier tube, which incorporates an efficient, low-electron-energy-spread photocathode as described herein.

[0013] The PMT and image sensors described herein have higher gain than prior art devices without dynodes or microchannel plates, and a faster response time than prior-art devices that use dynodes or microchannel plates. The image sensors described herein can have higher spatial resolution than prior art devices of similar gain. The PMT and image sensors described herein are simpler than many prior art devices and thus may be less expensive to manufacture and may have a longer operational life.

[0014] Small defects scatter low levels of light. More sensitive detectors allow dark-field inspection systems to detect smaller defects or particles. Detectors with better spatial resolution allow dark-field inspection systems to detect smaller defects or particles. Detectors with faster response time allow systems to run faster and reduce the inspection time, thereby increasing the value of those systems to end users.

**BRIEF DESCRIPTION OF THE DRAWINGS**

[0015] Figure 1 illustrates a known PMT including a photocathode, a focusing electrode, multiple dynodes, and an anode.

[0016] Figure 2 illustrates a PMT including a photocathode, an optional focusing electrode, and a photodiode all contained within an evacuated, sealed tube.

[0017] Figures 3A and 3B illustrate cross-sections of photocathodes suitable for use in the PMT and image sensor system described herein.

[0018] Figure 4 illustrates a cross-section of a photodiode suitable for use in a PMT described herein.

[0019] Figure 5 illustrates an exemplary electron-bombarded image sensor system.

[0020] Figure 6 illustrates a cross-section of an exemplary back-thinned image sensor suitable for use in the image sensor system shown in Figure 5.

[0021] Figures 7A and 7B illustrate exemplary dark-field inspection systems with multiple collection systems suitable for use with the PMT or image sensor described herein.

[0022] Figure 8 illustrates an exemplary surface inspection system that can be used for inspecting anomalies on a surface.

[0023] Figure 9 illustrates an exemplary inspection system configured to implement anomaly detection using both normal and oblique illumination beams.

[0024] Figure 10 illustrates the addition of a normal incidence laser dark-field illumination to an exemplary catadioptric imaging system.

**DETAILED DESCRIPTION OF THE DRAWINGS**

[0025] Figure 2 illustrates a PMT 200 including a photocathode 202, an optional focusing electrode 204, and a photodiode 205 all



contained within an evacuated, sealed tube 209. Notably, the photodiode 205 has a thin (for example, about 2 nm to 20 nm thick) pure boron coating on its surface facing the photocathode 205. The photodiode 205 is held at a positive voltage relative to the photocathode 202. For example, in one embodiment, the photodiode 205 may be at a voltage close to ground potential, whereas the photocathode 202 may be at a negative voltage relative to the photodiode 205 (e.g. a negative voltage between about 100 V and about 500 V). An incident photon 201 is absorbed by photocathode 202 and will likely cause an electron 203 to be ejected from the photocathode 202. Because of the potential difference between the photocathode 202 and the photodiode 205, the electron 203 will be accelerated towards the photodiode 205. Because of the pure boron coating on the surface of the photodiode 205 (described in detail below), any electron striking the photodiode 205 will have an almost 100% probability of being absorbed and of generating multiple electrons within the photodiode 205.

[0026] In some embodiments, the gap between photocathode 202 and photodiode 205 may be a few mm. In some preferred embodiments, the gap between photocathode 202 and photodiode 205 may be about 1 mm, or a few hundred  $\mu\text{m}$ .

[0027] In some embodiments, focusing electrode 204 may be used to ensure that a high percentage of the electrons 203 ejected from the photocathode 202 are directed towards to the photodiode 205. The focusing electrode 204 may be particularly useful when the gap between the photocathode 202 and the photodiode 205 is larger than about 1 mm. In some embodiments, when the gap between the photocathode 202 and the photodiode 205 is about 1 mm or smaller, the focusing electrode 204 may not be needed. The

focusing electrode 204 may comprise a cylinder, a mesh, or another electrode structure.

[0028] In preferred embodiments, photocathode 202 comprises a GaN photocathode or a boron-coated silicon photocathode. U.S. Patent Application 13/947,975, entitled "PHOTOCATHODE INCLUDING SILICON SUBSTRATE WITH BORON LAYER", filed on July 22, 2013 by Chuang et al. (Attorney Docket KLA-049 P3966), describes exemplary boron-coated silicon photocathodes suitable for use in the improved PMT described herein. In other embodiments, photocathode 202 may include one or more alkali metals or may comprise another photocathode material known in the art. Photocathode 202 may be a transmissive photocathode, as illustrated in Figure 2, or it may be a reflective photocathode.

[0029] Figures 3A and 3B illustrate cross-sections of photocathodes suitable for use in the PMT and image sensor system described herein.

[0030] Figure 3A illustrates a cross section of a GaN photocathode 300 including a plurality of layers on a substrate 301. The substrate 301 may include a sapphire substrate or a highly p-doped GaN substrate (for example, a doping concentration of about  $10^{18}$  atoms  $\text{cm}^{-3}$  or greater). In preferred embodiments, the substrate 301 may be between about 100  $\mu\text{m}$  and about 600  $\mu\text{m}$  thick. When the photocathode 300 is to be used in transmission mode, then the substrate 301 must be of high optical quality so that it transmits the wavelength range of interest. When the photocathode 300 is used in reflection mode, the optical quality of the substrate is less critical. For example, if the substrate 301 is a sapphire substrate and the photocathode 300 is to be

used in transmission mode for deep UV wavelengths, then very high purity sapphire should be used for the substrate 301.

[0031] In some transmission-mode photocathode embodiments, an anti-reflection layer 309 may be deposited on a first surface of the substrate 301. In some embodiments, the anti-reflection layer 309 may comprise one or more layers including magnesium fluoride ( $\text{MgF}_2$ ), silicon dioxide ( $\text{SiO}_2$ ), and/or hafnium oxide ( $\text{HfO}_2$ ).

[0032] In some embodiments, a buffer layer 302 is formed (e.g. grown or deposited) on a second surface of the substrate 301. When substrate 301 is a doped gallium nitride (GaN) substrate, then the buffer layer may not be needed. In preferred embodiments, the buffer layer 302 is a layer of Aluminum nitride (AlN) about 5 to 20 nm thick.

[0033] On top of the buffer layer 302 (or substrate 301, if the buffer layer 302 is not present) are a plurality of doped GaN layers 303 and 304. First doped GaN layer 303 can include a p-doped layer of GaN having a high doping concentration of about  $10^{18}$  atoms  $\text{cm}^{-3}$ . The preferred p-type dopant for first doped GaN layer 303 is magnesium (Mg). Second p-doped GaN layer 304 can include a much lower dopant concentration, e.g. a dopant concentration of approximately  $5 \times 10^{16}$  atoms  $\text{cm}^{-3}$ . In some embodiments, additional p-doped GaN layers may be placed between layers 303 and 304. Each of those additional layers should have a dopant concentration with intermediate values between those of layers 303 and 304 so as to form a step-wise decreasing dopant concentration from layer 303 to layer 304. For example, if layer 303 has a dopant concentration of about  $10^{18}$  atoms  $\text{cm}^{-3}$  and layer 304 has a dopant concentration of about  $5 \times 10^{16}$  atoms  $\text{cm}^{-3}$ , then a

layer (not shown) with a dopant concentration of about  $2 \times 10^{17}$  atoms  $\text{cm}^{-3}$  could be placed between the layers 303 and 304. In preferred embodiments, the thicknesses of the p-doped GaN layer should be similar to one another. The total thickness of all the p-doped GaN layers (e.g. if just two layers are used, then the sum of the thicknesses of layers 303 and 304) should be determined to maximize the quantum efficiency. For example, for a photocathode that has maximum sensitivity in the deep UV, the total thickness of all p-doped GaN layers may be about 180 nm. Exemplary GaN photocathodes are described in "Optimizing GaN photocathode structure for higher quantum efficiency", Optik, 123, pp756-768 (2012). In one embodiment, a standard Cs:O activation layer 306 can be deposited on the surface of the photocathode 300 from which electrons are ejected.

[0034] Figure 3B illustrates a cross section of a silicon photocathode 310. In transmission mode, photons 318 are incident on one surface of the photocathode 310 and electrons 319 are ejected from the opposite surface. In reflection mode, photons 318' are incident on the same surface as electrons are ejected from. In one embodiment, the silicon photocathode 310 includes silicon 311, preferably a single crystal of silicon. In some embodiments, the silicon photocathode 310 includes polycrystalline silicon or multi-crystalline silicon. Depending on the intended wavelength operating range of the photocathode, the silicon 311 may be between about 10 nm and about 100  $\mu\text{m}$  in thickness.

[0035] When intended for use as a transmission mode photocathode, the surface of the silicon on the side from which the light 318 is incident may, optionally, be coated with an anti-reflection (AR) layer 313. An exemplary AR layer 313 may

include one or more layers of transparent or semi-transparent materials, such as  $\text{MgF}_2$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{HfO}_2$ . For some embodiments intended for operation at deep UV or vacuum UV wavelengths in transmission mode, a thin pure boron layer 312 may be present between the AR layer 313 and the silicon 311. This pure boron layer 312 may be between about 2 nm and 4 nm thick.

[0036] The silicon 311 is coated with a thin pure boron layer 314 on the surface from which electrons are ejected. The pure boron layer 314 is preferably between about 2 nm and 20 nm thick. In one embodiment, a standard Cs:O (cesium:oxygen) activation layer 316 can be deposited on the surface of the photocathode from which electrons are ejected.

[0037] An exemplary silicon photocathode structure suitable for use in a PMT or an electron-bombarded image sensor system is described in the above-cited U.S. Patent Application 13/947,975, entitled "PHOTOCATHODE INCLUDING SILICON SUBSTRATE WITH BORON LAYER", filed on July 22, 2013 .

[0038] Figure 4 illustrates a cross-section of a photodiode 400 suitable for use in a PMT described herein. Note that although this diode is referred to herein as a photodiode, it is to be understood that, in the PMT disclosed herein, it is actually detecting electrons and converting incident electrons into an electrical current, rather than directly detecting photons. The structure, function, and associated circuits are similar to those used for photodiodes, so it is convenient to refer to it as a photodiode. Also note that this cross section is not drawn to scale, but is merely intended to illustrate important aspects of the structure of the photodiode device as used in the PMT described herein.

[0039] Photodiode 400 comprises a pn or pin junction formed by a p-doped semiconductor layer 404 (anode) contacting an n-doped semiconductor layer 403 (cathode). In preferred embodiments, the n-doped semiconductor layer 403 is lightly n-doped (designated as N-doped in Figure 4). The n doping may be done with phosphorous, arsenic, or another n-type dopant. The p doping for p-doped semiconductor layer 404 may be done with boron or another p-type dopant. A pure boron layer 406 is formed on a surface of the p-doped semiconductor layer 404. In some embodiments, a separate p implant or doping step may be unnecessary because enough boron may diffuse into the surface of the p-doped semiconductor layer 404 during the deposition of pure boron layer 406.

[0040] Electrical connections 401 are made to the anode and cathode. To have a low resistance contact to the cathode, a highly n-doped semiconductor layer 402 (designated N<sup>+</sup> doped in Figure 4) may be formed on a surface of the N-doped semiconductor layer 403. To have a low resistance contact to the anode, a capping layer 408 comprising a thin (such as between about 1 nm and about 20 nm thick) conductive material such as semi-metal (e.g. titanium nitride (TiN)) or a metal may be formed on a surface of the pure boron layer 406. In some embodiments, the capping layer 408 may be omitted because the conductivity of the surface of the p-doped semiconductor layer 404 is sufficient. This may be the case when the PMT is intended only to operate with low light levels and never exposed to high light levels, because the photodiode current will always remain relatively low in such cases. When the PMT may be exposed to high light levels, even occasionally, the capping layer 408 can provide additional advantages of reducing charge up of the anode surface of the

photodiode 400, and of protecting the pure boron layer 406 from being sputtered by incident electrons 409.

[0041] In one embodiment, a thick pure boron layer 406 (e.g. approximately 2 nm to 20 nm) can be directly formed on top of the p-doped semiconductor layer 404. The pure boron layer 406 allows low energy electrons to penetrate into the p-doped semiconductor layer 404. It is important that the pure boron layer 406 cover the entire area where electrons will be incident and be pinhole free, thereby preventing the growth of a native oxide film on the surface of the semiconductor. Note that a native oxide film would charge up when hit by electrons and could repel low energy electrons, thereby greatly reducing the sensitivity of the photodiode when the PMT operates at a low voltage. Operation of the PMT at a low voltage is important because it allows a small gap between the photocathode and the photodiode, which speeds the response time of the PMT as the electrons take less time to cross that gap. Furthermore, a low voltage difference between the photocathode and photodiode 400 minimizes sputtering and damage to the pure boron layer 406 and the p-doped semiconductor layer 404 that can be caused by high energy electrons.

[0042] The quality of the pure boron layer 406 is critical to the optimal performance of the photodiode. The surface of p-doped semiconductor layer 404 should be clean of contaminants and native oxide prior to deposition of the pure boron layer. More details on boron deposition can be found in "Chemical vapor deposition of a-boron layers on silicon for controlled nanometer-deep p+-n junction formation," Sarubbi et al., J. Electron. Material, vol. 39, pp. 162-173 (2010). In preferred embodiments, the photodiode 400 is operated reverse biased (i.e. the anode is

slight negative relative to the cathode) in order to have a fast response and low dark current.

[0043] Figure 5 illustrates an exemplary electron-bombarded image sensor system 501. In this embodiment, the whole assembly can be contained in a sealed tube 505 (e.g. substantially similar to the sealed tube of standard image intensifier and electron-bombarded CCD (EBCCD) devices). A top surface 507 of the tube 505 can include a window that is transparent at the wavelengths of interest. For UV sensitive electron-bombarded image sensors, this window preferably comprises a very pure grade of quartz, fused silica or alumina (sapphire). In some preferred embodiments, the outside surface of the window is coated with a UV anti-reflection coating. Such a coating might comprise a single layer of a low index material, such as  $\text{MgF}_2$ , or might comprise a multi-layer coating.

[0044] Coated on the inside surface of the window, or placed immediately adjacent to that inside surface, is a photocathode 504. The photocathode material may be substantially similar to any photocathode material known in the art for use in photomultiplier, image intensifier, or prior-art EBCCD detectors. In preferred embodiments, the photocathode 504 may comprise one or more alkali metals such as cesium, and/or may comprise a semiconductor such as GaN, GaAs, or silicon. The photocathode 504 can be held at a negative voltage 503 relative to a solid-state image sensor 502, which is positioned near the bottom surface of sealed tube 505. In some embodiments, the negative voltage 503 may be approximately 500 V; in other embodiments, it may be a few hundred volts or approximately 1000 V. In preferred embodiments, the negative voltage 503 is between 100 V and 1500 V.



[0045] The solid-state image sensor 502 can be a thinned CCD or CMOS image sensor oriented so that the electrons impinge first on its back-side surface. The back-side of solid-state image sensor 502 includes a layer of boron deposited directly on the epi layer of the image array. In some embodiments, a thin (few nm) layer of a conductive material, such as a refractory metal, is deposited on the boron layer to prevent charge-up of the sensor surface. A refractory metal such as titanium, tungsten, tantalum, rhodium, ruthenium, vanadium or chromium, has advantages compared with non-refractory metals because refractory metals' hardness makes them resistant to sputtering by the electrons, and they are relatively resistant to oxidation at room temperature. In some embodiments, the solid-state image sensor 502 is a time-delay integration (TDI) CCD. In some embodiments, the solid-state image sensor 502 comprises a linear array of electron-sensitive elements. In other embodiments, the solid-state image sensor 502 comprises a two-dimensional array of electron sensitive elements. In some preferred embodiments, the solid-state image sensor 502 is held close to ground potential (shown).

[0046] When light 510 is incident on the electron-bombarded image sensor system 501, one or more photoelectrons 520 are emitted from the photocathode 504. These photoelectrons are emitted in substantially all directions, but they are accelerated towards the solid-state image sensor 502 by the potential difference between the photocathode 504 and the solid-state image sensor 502. In preferred embodiments, the gap between the photocathode 504 and the solid-state image sensor 502 is less than 1 mm. In some embodiments, the gap is approximately 500  $\mu\text{m}$ .

[0047] Incorporating the solid-state image sensor 502 having one of the structures and/or fabricated in accordance with any of the methods described herein enables the electron-bombarded image sensor system 501 to operate with a low potential difference between the photocathode 504 and the solid-state image sensor 502, and yet have high gain because electrons are more easily able to penetrate through the boron layer (of the image sensor 502) than through a silicon dioxide layer. Because boron-doped silicon, boron silicide, and boron are all at least partially conductive, charging of the surface under electron bombardment is minimized or avoided. The sensitivity to charge up can be further reduced by a conductive or metallic layer on top of the boron layer as described herein.

[0048] In prior art EBCCD sensors, the gap between the photocathode and the image sensor is typically 1-2 mm. Such a large gap allows significant transverse motion of the electrons as they travel from the photocathode to the image sensor due to energy of the electrons as they emerge from the photocathode. A gap of 1-2 mm or more is necessary because of the large potential difference between the photocathode and the image sensor (typically about 2000 V or more). Reducing the potential difference between the photocathode and the image sensor allows a smaller gap to be used. Furthermore, the lower energy of the electrons means that there is less spreading of the electrons created within the solid-state image sensor.

[0049] The low energy of the electrons arriving at the image sensor 502 means that the probability of atoms being ablated from its surface is low to zero. Furthermore, the energy of the electrons arriving at the solid state image sensor 502 is not enough to generate X-rays from the silicon, thereby avoiding the

generation of spurious signals in nearby pixels of the image sensor 502.

[0050] Collisions of low energy electrons with residual gas atoms in the vacuum created in the sealed tube 505 will generate fewer ions as compared with high energy electrons. Furthermore, due to the low potential difference between the photocathode 504 and the image sensor 502, those ions will have less kinetic energy when they strike the photocathode and will ablate less photocathode material.

[0051] More details of the image sensor system 501 can be found in U.S. Published Application 2013/0264481, entitled "Back-illuminated sensor with boron layer", filed March 10, 2013 and published October 10, 2013. Additional details of electron-bombarded image sensors that can be incorporated into the image sensor system 501 can be found in U.S. Published Application 2013/0148112, entitled "Electron-bombarded charge-coupled device and inspection systems using EBCCD detectors", filed on December 10, 2012 and published June 13, 2013. Both of these applications are incorporated by reference herein.

[0052] Figure 6 illustrates a cross-section of an exemplary back-thinned image sensor 600 suitable for use in image sensor system 501 (Figure 5). In one embodiment, an epitaxial (epi) layer 602 is formed on a front side of a substrate 601. In one embodiment, the substrate 601 is a p+ (i.e. highly p doped) substrate, and the epi layer 602 is a p- (i.e. a layer with a low concentration of p dopant) epi layer. One or more gate dielectric layers, such as a gate oxide layer 603 and a silicon nitride ( $\text{Si}_3\text{N}_4$ ) gate layer 604 may be formed on the epi layer 602. Note that depending on the type of image sensor technology, each

of the gate dielectric layers may comprise one, two, or three layers. Front-side circuit elements 605 may be formed on gate layer 604. Forming the front-side circuit elements 605 may include implanting or doping portions of the front side of the epi layer 602 and may involve patterning the gate layers 603 and 604. Front-side metal (i.e. interconnect) 607 can be formed on the front-side circuit elements 605.

[0053] As shown in Figure 6, the substrate 601 is thinned from its back-side surface, at least in certain areas, so that electrons can impinge directly on the epi layer 602. In one embodiment, a pure boron layer 606 (e.g. between about 2 nm and about 20 nm thick) is formed on thinned substrate 601 and exposed portions of the epi layer 602. In some embodiments a capping layer 608 can be formed on the pure boron layer 606. The capping layer 608 can include a thin conductive film, such a layer between about 1nm and about 20 nm thick of a metal or semi-metal.

[0054] More details and alternative embodiments of the image sensor 600 as well as methods of fabricating the image sensor 600 can be found in U.S. Patent Application 13/792,166, entitled "Back-illuminated sensor with boron layer", filed March 10, 2013.

[0055] Figures 7A and 7B illustrate an exemplary dark-field inspection system with multiple collection systems suitable for use with the PMT or image sensor described herein.

[0056] Figure 7A illustrates an exemplary surface inspection apparatus 700 that includes an illumination system 701 and a collection system 710 for inspecting areas of a sample surface 711. As shown in Figure 7A, a laser system 720 directs a light beam 702 through a lens 703. The lens 703 is oriented so that

its principal plane is substantially parallel to the surface 711 and, as a result, an illumination line 705 is formed on the surface 711 in the focal plane of the lens 703. In addition, the light beam 702 and a focused beam 704 are directed at a non-orthogonal angle of incidence to the surface 711. In particular, the light beam 702 and the focused beam 704 may be directed at an angle between about 1 degree and about 85 degrees from a normal direction to the surface 711. In this manner, the illumination line 705 is substantially in the plane of incidence of the focused beam 704.

[0057] The collection system 710 includes a lens 712 for collecting light scattered from the illumination line 705 and a lens 713 for focusing the light coming out of the lens 712 onto a device 714. The device 714 may include an array of light sensitive detectors (such as an array of PMTs) or an electron-bombarded image sensor. In preferred embodiments, the PMTs or electron-bombarded image sensor comprise a boron coated detector, such as a boron-coated photodiode, or a boron-coated image sensor as described herein. In preferred embodiments, the PMT or image sensor may further comprise a GaN or silicon photocathode as described herein. The linear array of detectors within the device 714 can be oriented parallel to the illumination line 715. In one embodiment, multiple collection systems can be included, wherein each of the collection systems includes similar components, but differ in orientation.

[0058] For example, Figure 7B illustrates an exemplary array of collection systems 731, 732, and 733 for a surface inspection apparatus (wherein its illumination system, e.g. similar to that of illumination system 701, is not shown for simplicity). First optics in the collection system 731 collect light scattered in a

first direction from the surface of the surface 711. Second optics in the collection system 732 collect light scattered in a second direction from the surface 711. Third optics in the collection system 733 collect light scattered in a third direction from the surface 711. Note that the first, second, and third paths are at different angles of reflection to the surface 711. A platform 735 supporting the sample can be used to cause relative motion between the optics and surface 711 so that the whole surface can be scanned. At least one of the collection systems 731, 732, and 733 may include an array of light sensitive detectors (such as an array of PMTs) or an electron-bombarded image sensor as described herein. U.S. Patent 7,525,649, which issued on April 28, 2009 and is incorporated by reference herein, describes the surface inspection apparatus 700 and other multiple collection systems in further detail.

[0059] Figure 8 illustrates an exemplary surface inspection system 800 that can be used for inspecting anomalies on a surface 801. In this embodiment, the surface 801 can be illuminated by a substantially stationary illumination device portion of a laser system 830, which generates a laser beam. The output of the laser system 830 can be consecutively passed through polarizing optics 821, a beam expander and aperture 822, and beam-forming optics 823 to expand and focus the beam.

[0060] The resulting focused laser beam 802 is then reflected by a beam folding component 803 and a beam deflector 804 to direct the beam 805 towards the surface 801. In a preferred embodiment, the beam 805 is substantially normal or perpendicular to the surface 801, although in other embodiments, the beam 805 may be at an oblique angle to the surface 801.

[0061] In one embodiment, the beam 805 is substantially perpendicular or normal to the surface 801 and the beam deflector 804 reflects the specular reflection of the beam from the surface 801 towards the beam turning component 803, thereby acting as a shield to prevent the specular reflection from reaching detectors (described below). The direction of the specular reflection is along line SR, which is normal to the surface 801 of the sample. In one embodiment where the beam 805 is normal to the surface 801, this line SR coincides with the direction of the beam 805, where this common reference line or direction is referred to herein as the axis of surface inspection system 800. Where the beam 805 is at an oblique angle to the surface 801, the direction of specular reflection SR would not coincide with the incoming direction of the beam 805; in such instance, the line SR indicating the direction of the surface normal is referred to as the principal axis of the collection portion of the surface inspection system 800.

[0062] Light scattered by small particles is collected by a mirror 806 and directed towards an aperture 807 and a detector 808. Light scattered by large particles are collected by lenses 809 and directed towards an aperture 810 and a detector 811. Note that some large particles will scatter light that is also collected and directed to the detector 808, and similarly some small particles will scatter light that is also collected and directed to the detector 811, but such light is of relatively low intensity compared to the intensity of scattered light the respective detector is designed to detect. In one embodiment, the either or both detectors 808 and 811 can include a PMT or an array of PMTs as described herein. In another embodiment, either or both detectors 808 and 811 include an electron-bombarded image sensor as described herein. In one embodiment, inspection system

can be configured for use in detecting defects on unpatterned wafers. U.S. Patent 6,271,916, which issued on August 7, 2011 and is incorporated by reference herein, describes surface inspection system 800 in further detail.

[0063] Figure 9 illustrates an exemplary inspection system 900 configured to implement anomaly detection using both normal and oblique illumination beams. In this configuration, a laser system 930 can provide a laser beam 901. A lens 902 focuses the beam 901 through a spatial filter 903 and a lens 904 collimates the beam and conveys it to a polarizing beam splitter 905. A beam splitter 905 passes a first polarized component to a normal illumination channel 906 and a second polarized component to an oblique illumination channel 912, where the first and second components are orthogonally polarized. In the normal illumination channel 906, the first polarized component is focused by optics 907 and reflected by a mirror 908 towards a surface of a sample 909. The radiation scattered by sample 909 is collected and focused by a paraboloidal mirror 910 to a detector 911. The detector 911 includes a PMT as described herein.

[0064] In the oblique illumination channel 912, the second polarized component is reflected by a beam splitter 905 to a mirror 913, which reflects such beam through a half-wave plate 914 and focused by optics 915 to the sample 909. Radiation originating from the oblique illumination beam in the oblique illumination channel 912 and scattered by the sample 909 is also collected by a paraboloidal mirror 910 and focused to a detector 911, which has a pinhole entrance. The pinhole and the illuminated spot (from the normal and oblique illumination channels on the sample 909) are preferably at the foci of a



paraboloidal mirror 910. Note that curved mirrored surfaces having shapes other than paraboloidal shapes may also be used.

[0065] The paraboloidal mirror 910 collimates the scattered radiation from the sample 909 into a collimated beam 916. The collimated beam 916 is then focused by an objective 917 through an analyzer 918 to the detector 911. The detector 911 may include one or more light sensitive detectors, such as one or more PMTs or electron-bombarded image sensors as described herein. An instrument 920 can provide relative motion between the beams and the sample 909 so that spots are scanned across the surface of the sample 909. U.S. Patent 6,201,601, which issued on March 13, 2001 and is incorporated by reference herein, describes inspection system 900 in further detail.

[0066] Figure 10 illustrates the addition of a normal incidence laser dark-field illumination to an exemplary catadioptric imaging system 1000. The dark-field illumination includes a UV laser 1001, adaptation optics 1002 to control the illumination beam size and profile on the surface being inspected, an aperture and window 1003 in a mechanical housing 1004, and a prism 1005 to redirect the laser along the optical axis at normal incidence to the surface of a sample 1008. The prism 1005 also directs the specular reflection from surface features of the sample 1008 and reflections from the optical surfaces of an objective 1006 along the optical path to an image plane 1009. Lenses for the objective 1006 can be provided in the general form of a catadioptric objective, a focusing lens group, and a zooming tube lens section. In a preferred embodiment, the image plane 1009 includes one or more light sensitive detectors, such as one or more PMTs or electron-bombarded image sensors, as described herein. U.S. Patent 5,999,310, which issued on

December 7, 1999 and U.S. Publication 2007/0002465, which published on January 4, 2007 describe catadioptric imaging system 1000 in further detail. Both the patent and the publication are incorporated by reference herein.

[0067] The various embodiments of the structures, methods, and systems described above are illustrative only of the principles of this invention and are not intended to limit the scope of the invention to the particular embodiments described. For example, the photocathode of the PMT or electron-bombarded image may comprise any type of photocathode known in the art. In another example, a PMT or electron-bombarded image sensor as described herein may be incorporated into any metrology or inspection system, not limited to the specific systems described herein. In yet another example, an inspection system incorporating a PMT or electron-bombarded image sensor as described herein may use a broad-band light source such as a laser-pumped plasma light source or an arc lamp, rather than a laser as in the illustrative examples herein. Thus, the invention is limited only by the following claims and their equivalents.

## CLAIMS

1. A photomultiplier tube comprising:  
a semiconductor photocathode; and  
a photodiode including:  
    a p-doped semiconductor layer;  
    a n-doped semiconductor layer formed on a first surface  
of the p-doped semiconductor layer to form a diode; and  
    a pure boron layer formed on a second surface of the p-  
doped semiconductor layer.
2. The photomultiplier tube of claim 1 wherein the  
semiconductor photocathode comprises gallium nitride.
3. The photomultiplier tube of claim 2, wherein the  
semiconductor photocathode further comprises one or more p-doped  
gallium nitride layers.
4. The photomultiplier tube of claim 1 wherein the  
semiconductor photocathode comprises silicon.
5. The photomultiplier tube of claim 4, wherein the  
semiconductor photocathode further comprises a pure boron coating  
on at least one surface.
6. The photomultiplier tube of claim 1, wherein a gap  
between the semiconductor photocathode and the photodiode is less  
than about 1 mm.
7. The photomultiplier tube of claim 6 wherein a gap  
between the semiconductor photocathode and the photodiode is less  
than about 500  $\mu\text{m}$ .

8. A system for inspecting a sample, the system comprising:  
a laser system for generating light;  
first components for directing the light to the sample;  
one or more detectors; and  
second components for directing light from the sample to the  
one or more detectors,  
at least one detector including a photomultiplier tube, the  
photomultiplier tube comprising:  
a semiconductor photocathode; and  
a photodiode including:  
a p-doped semiconductor layer;  
a n-doped semiconductor layer formed on a first surface  
of the p-doped semiconductor layer to form a diode; and  
a pure boron layer formed on a second surface of the p-  
doped semiconductor layer.

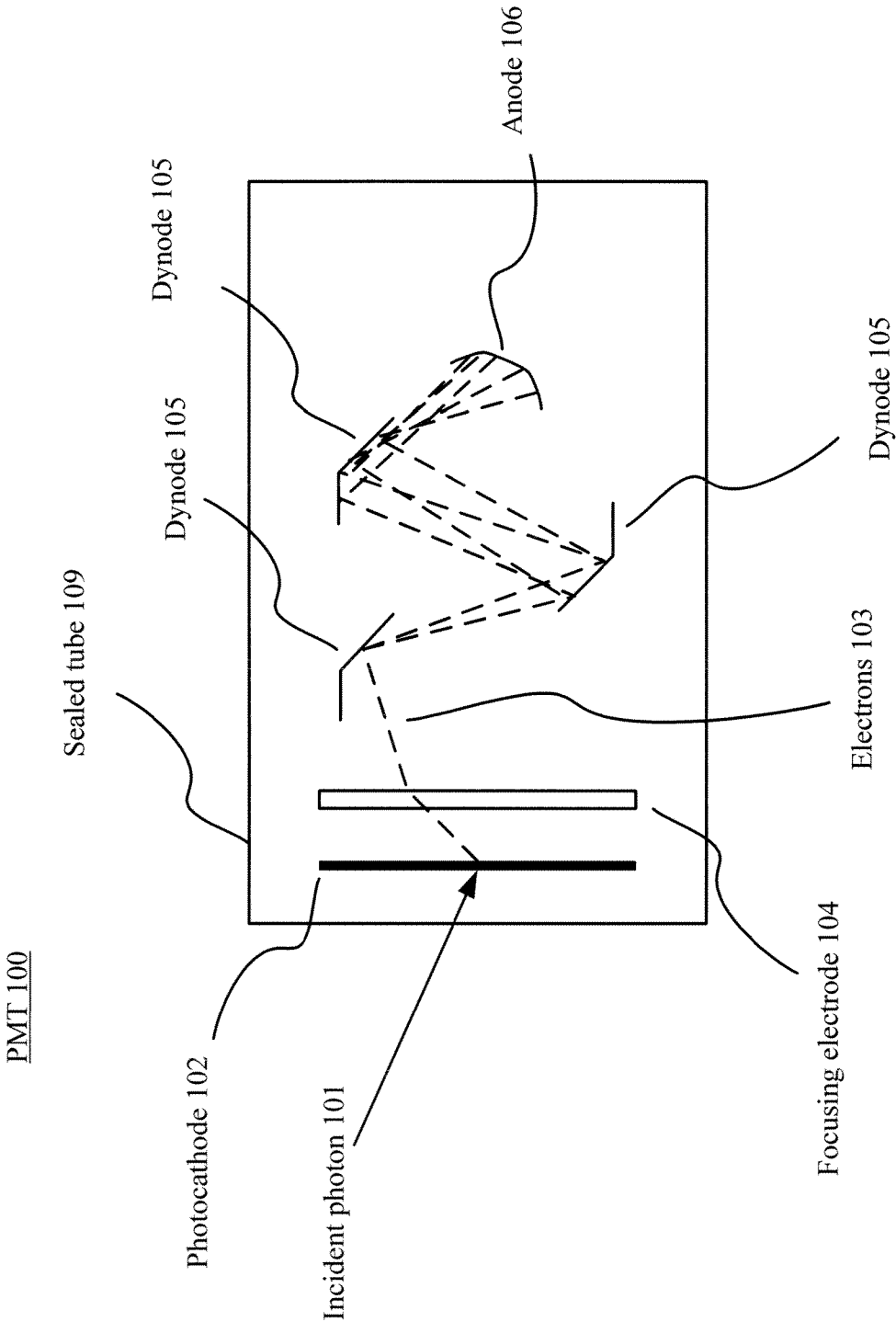


Figure 1  
Prior Art

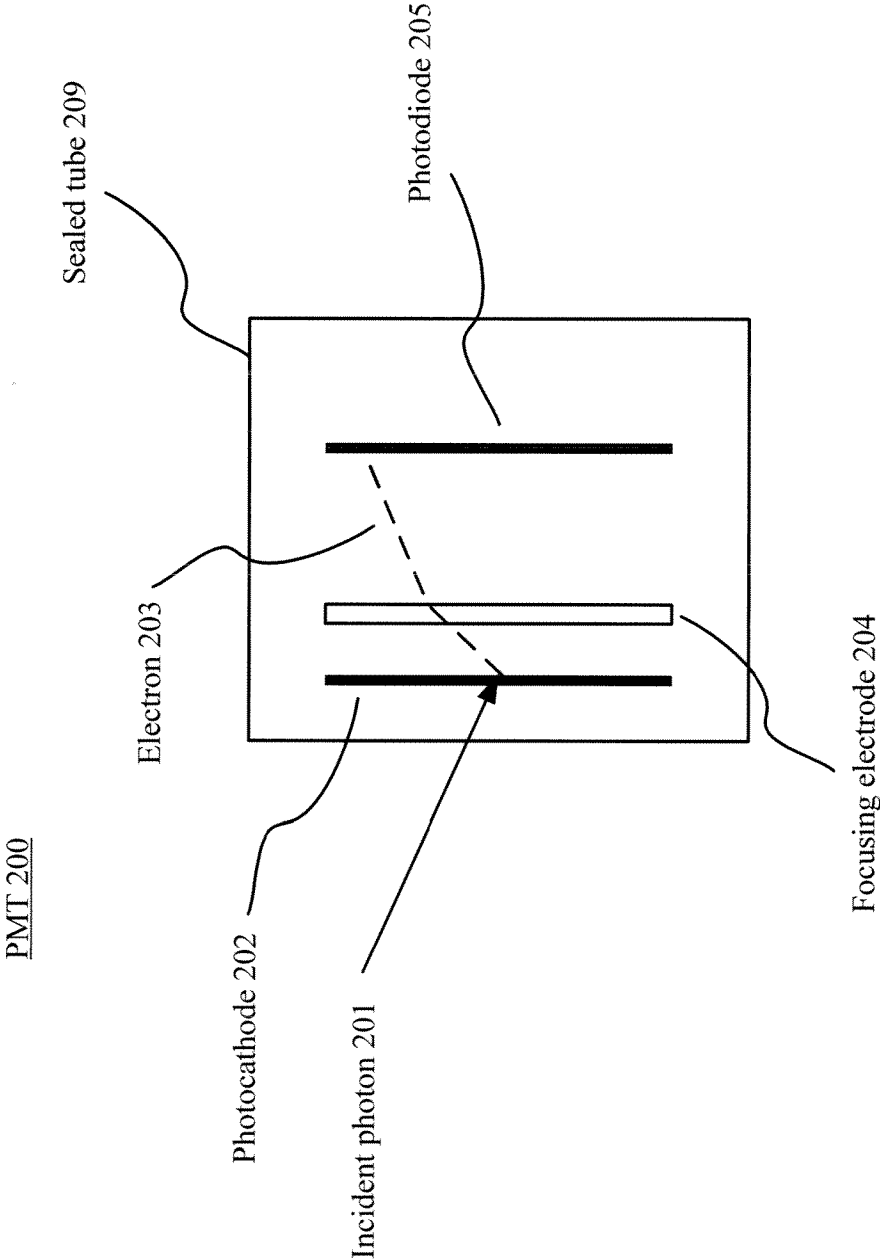


Figure 2

GaN Photocathode 300

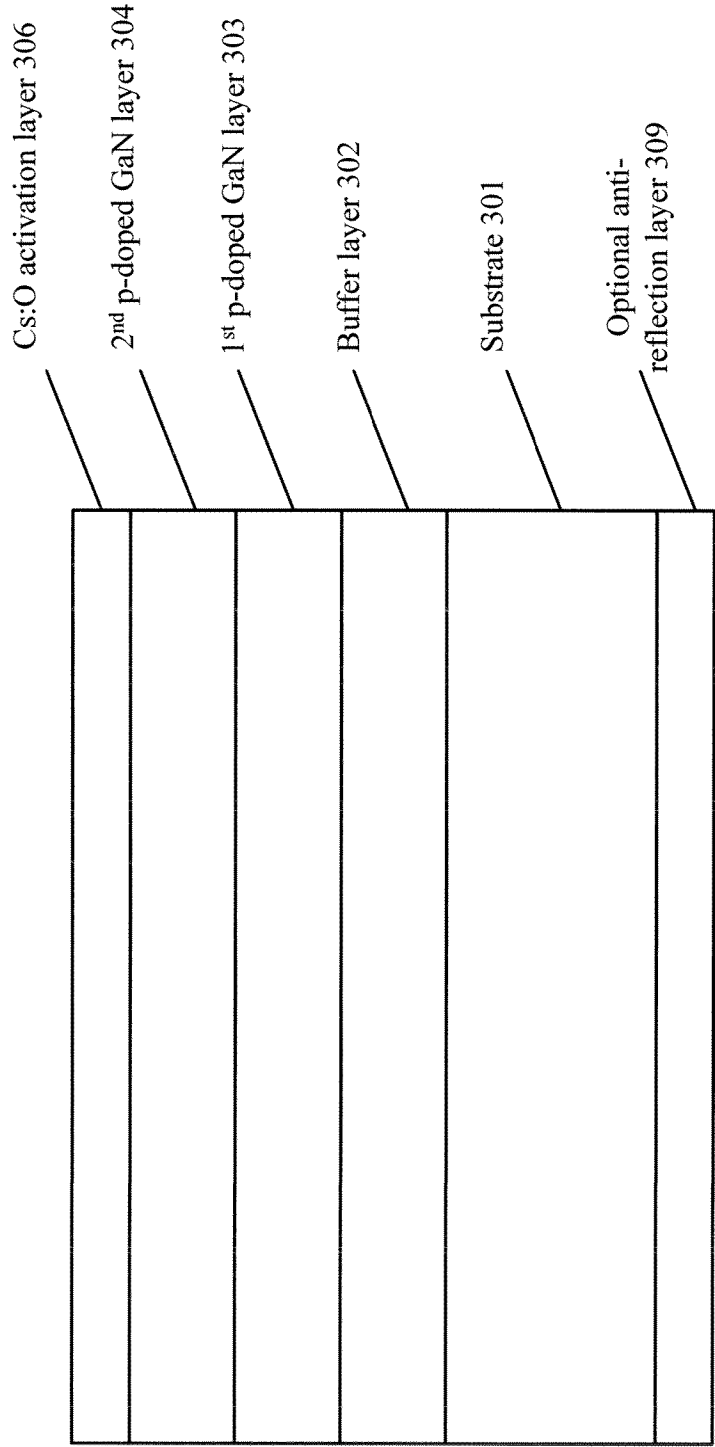
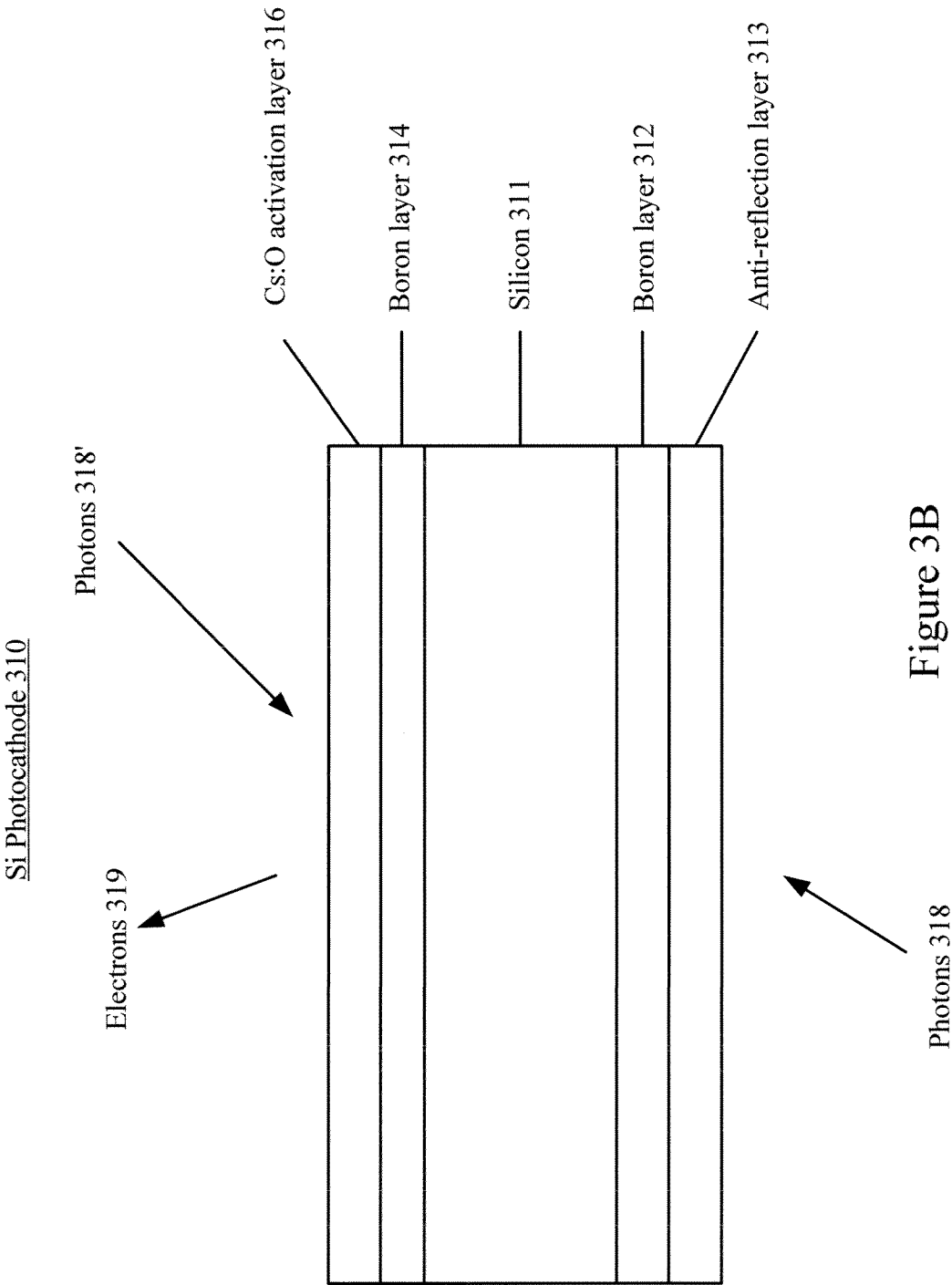


Figure 3A





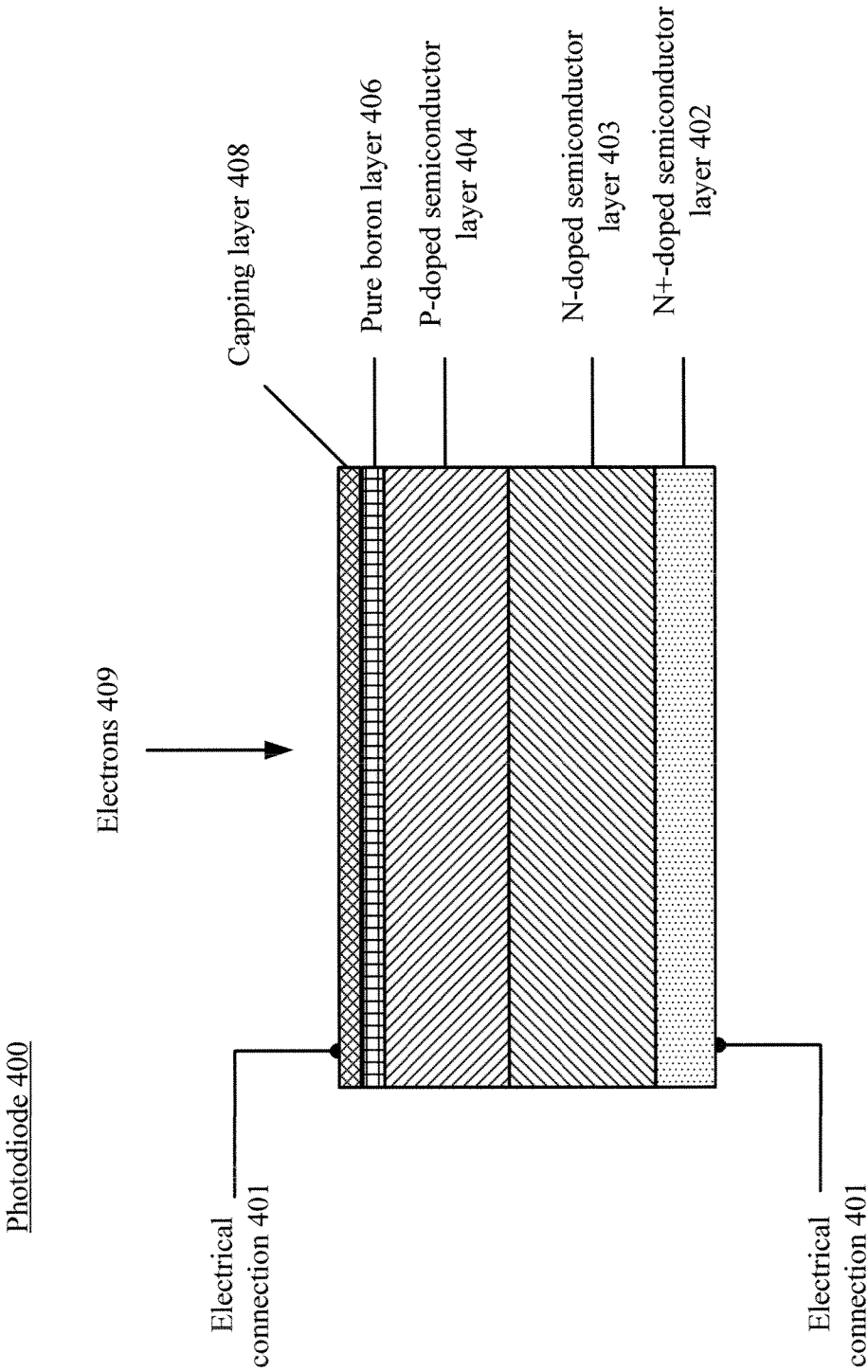


Figure 4

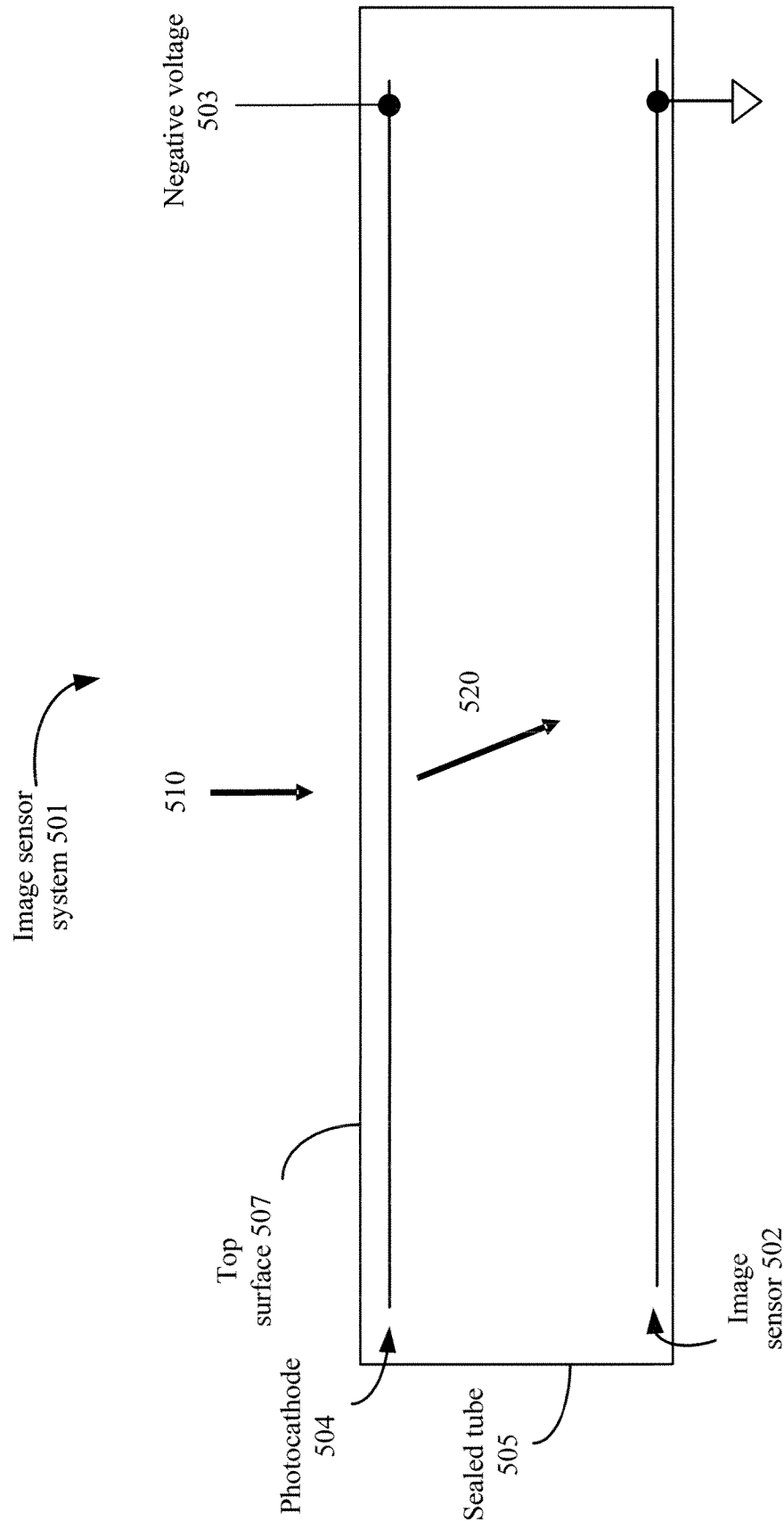


Figure 5

Image sensor 600

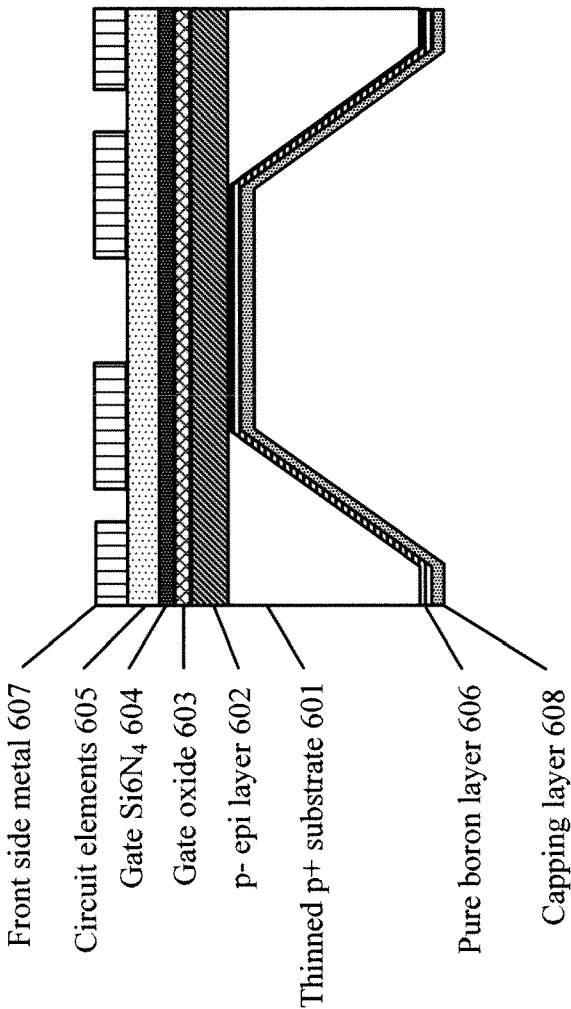


Figure 6

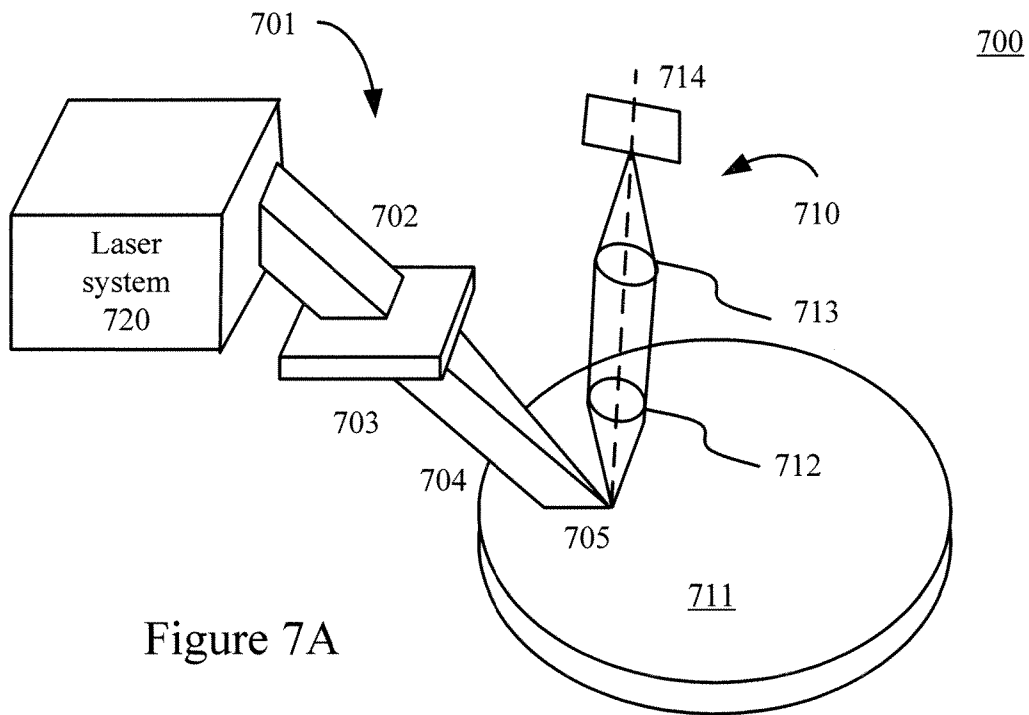


Figure 7A

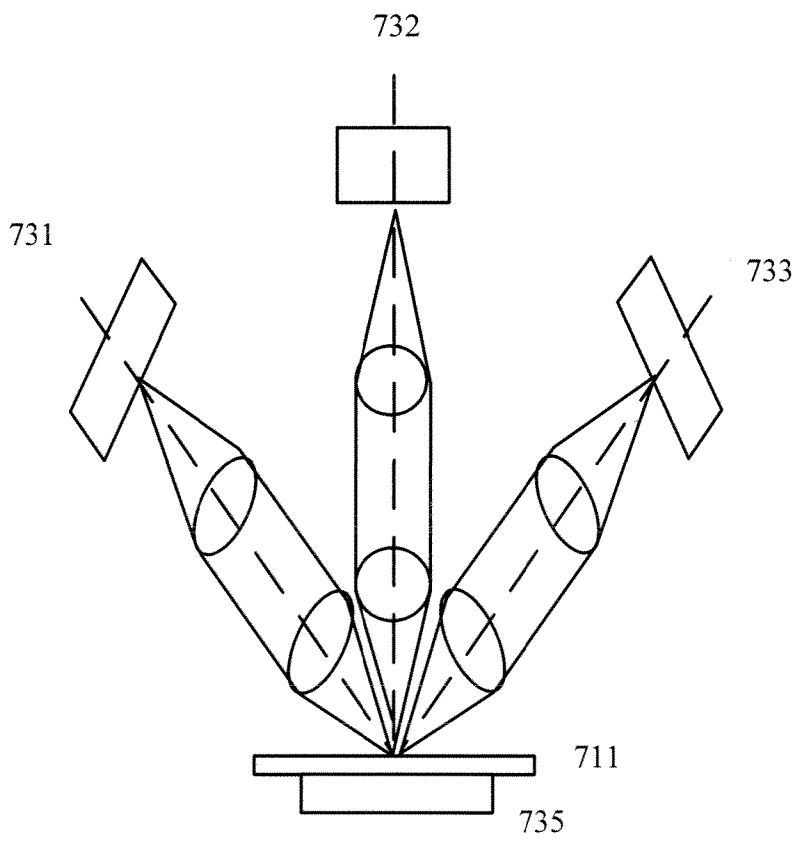


Figure 7B

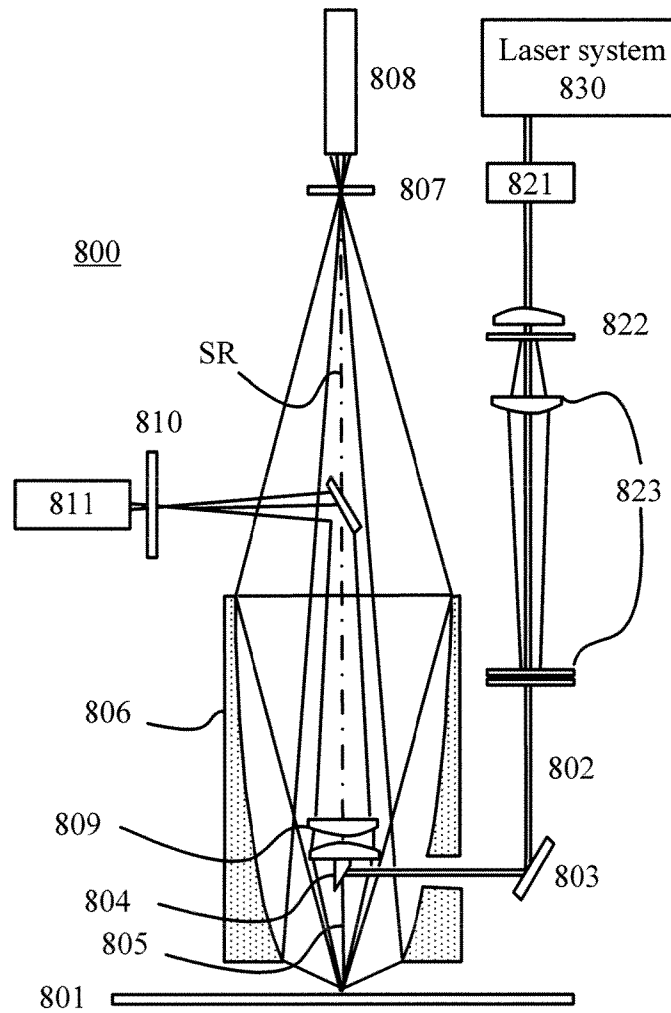


Figure 8

900

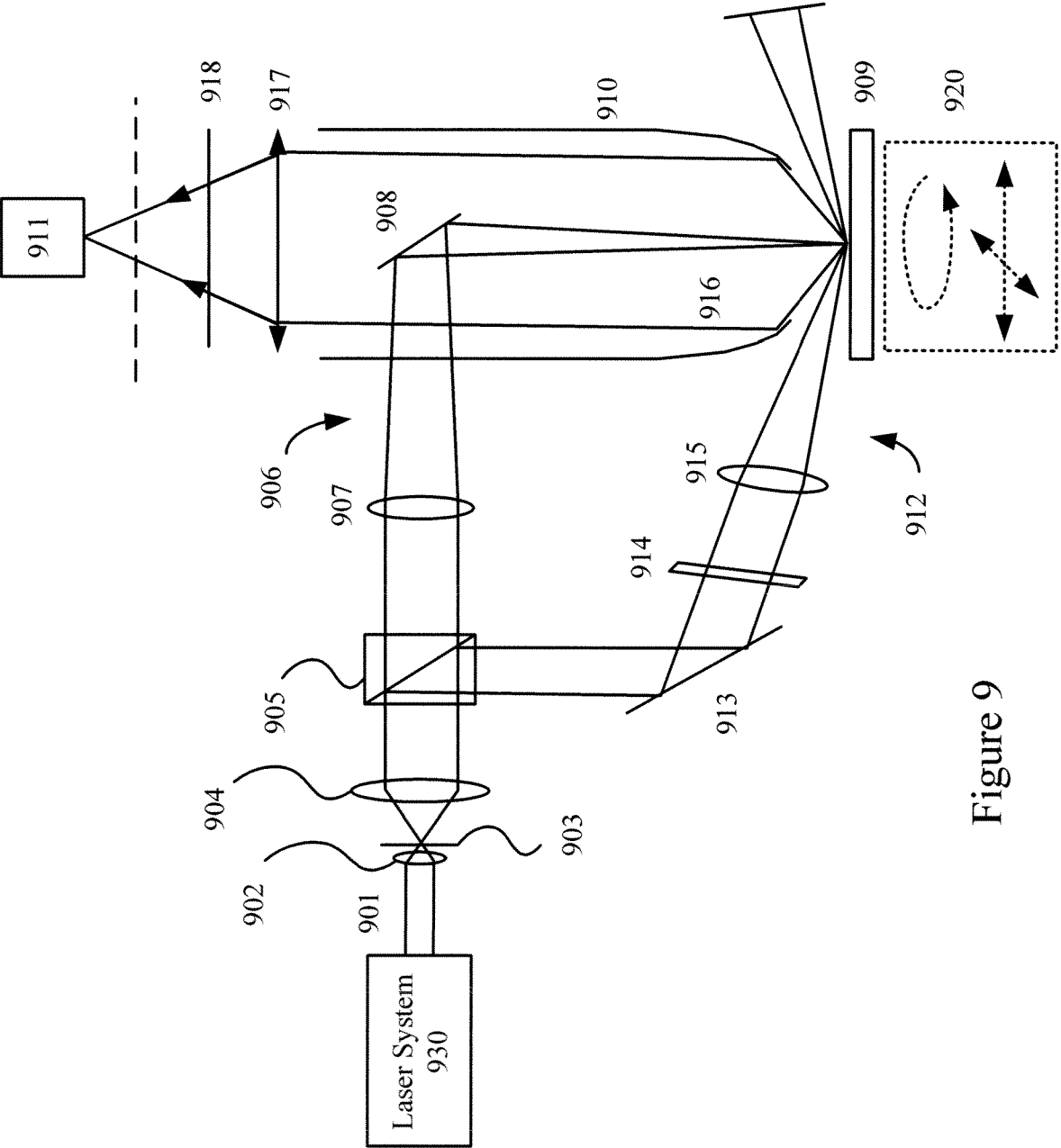


Figure 9

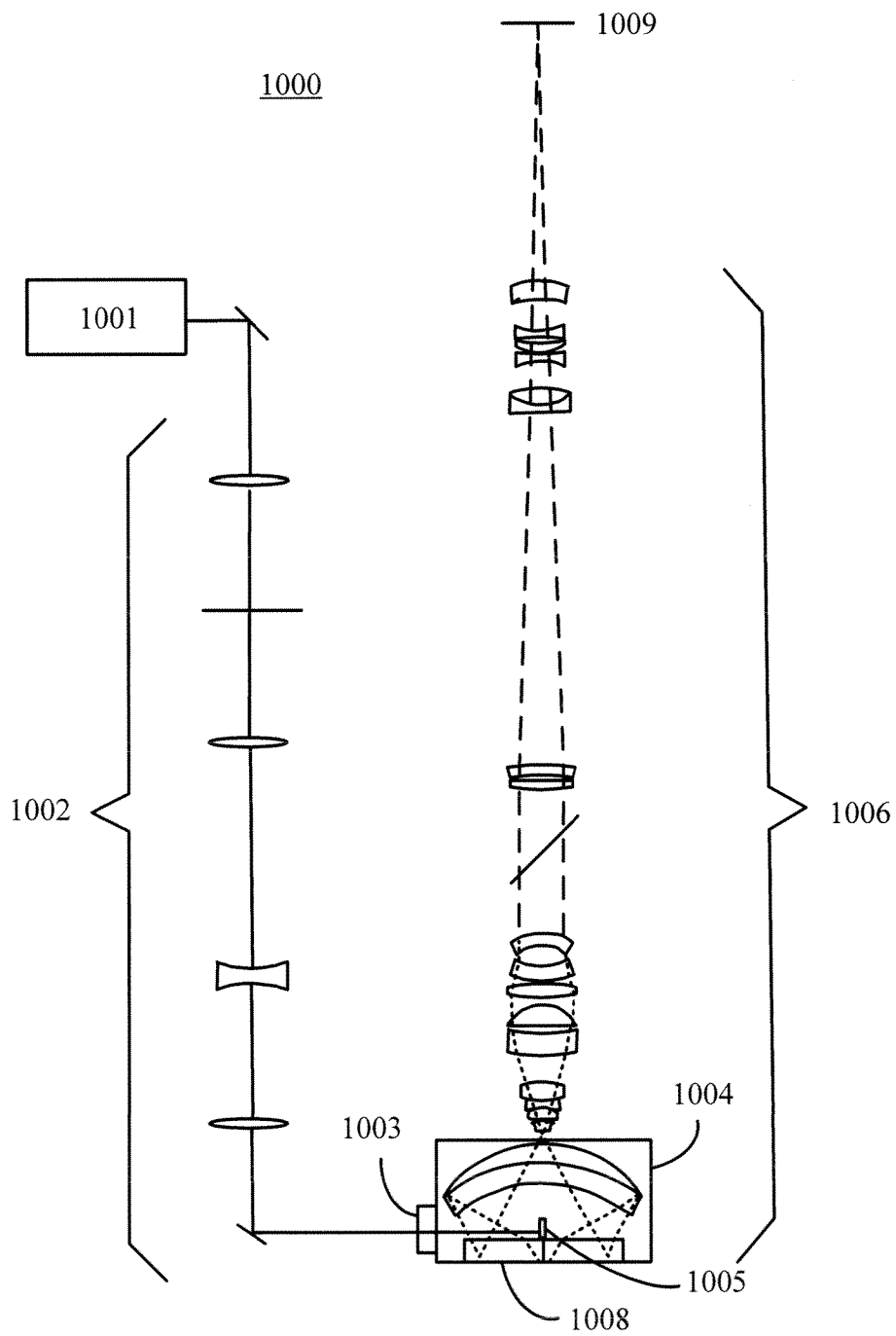


Figure 10

## INTERNATIONAL SEARCH REPORT

International application No.  
**PCT/US2014/032579****A. CLASSIFICATION OF SUBJECT MATTER****H01L 27/146(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

H01L 27/146; H01L 31/0264; H01L 31/0336; H01L 31/0224; H01L 31/12; H01L 31/18; G01N 21/00; H01L 27/14

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) &amp; Keywords: photomultiplier tube, image sensor, photodiode, photocathode, boron

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2012-0012811 A1 (MICHAEL E. DEFLUMERE et al.) 19 January 2012 See paragraphs [0022], [0030], claim 6 and figure 1.	1-3
A		4-8
Y	US 2011-0169116 A1 (LIS KAREN NANVER et al.) 14 July 2011 See paragraphs [0077], [0079] and figure 1.	1-3
A		4-8
A	US 6201601 B1 (MEHDI VAEZ-IRAVANI et al.) 13 March 2001 See column 5, lines 40-64, claim 1 and figure 2A.	1-8
A	JP 2004-031452 A (MITSUBISHI ELECTRIC CORP.) 29 January 2004 See paragraphs [0015]-[0017], claim 1 and figure 1.	1-8
A	US 5146296 A (GERALD C. HUTH) 08 September 1992 See column 9, lines 18-44, claim 1 and figure 1.	1-8



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

14 August 2014 (14.08.2014)

Date of mailing of the international search report

**14 August 2014 (14.08.2014)**

Name and mailing address of the ISA/KR

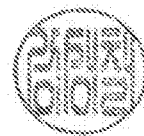
International Application Division  
Korean Intellectual Property Office  
189 Cheongsu-ro, Seo-gu, Daejeon Metropolitan City, 302-701,  
Republic of Korea

Facsimile No. +82-42-472-7140

Authorized officer

KANG, Sung Chul

Telephone No. +82-42-481-8405





**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/US2014/032579**

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2012-0012811 A1	19/01/2012	EP 2380047 A1	26/10/2011
		EP 2380047 A4	24/10/2012
		JP 2012-516023 A	12/07/2012
		US 2014-0034813 A1	06/02/2014
		US 8581228 B2	12/11/2013
		WO 2010-085478 A1	29/07/2010
US 2011-0169116 A1	14/07/2011	CN 102130218 A	20/07/2011
		EP 2346094 A1	20/07/2011
		EP 2346095 A2	20/07/2011
		EP 2346095 A3	27/07/2011
		JP 2011-145292 A	28/07/2011
		US 8450820 B2	28/05/2013
US 6201601 B1	13/03/2001	AU 1998-94000 A1	05/04/1999
		AU 9400098 A	05/04/1999
		DE 69819929 D1	24/12/2003
		DE 69819929 T2	11/11/2004
		DE 69828827 D1	03/03/2005
		DE 69828827 T2	05/01/2006
		DE 69840532 D1	19/03/2009
		EP 1023582 A1	02/08/2000
		EP 1023582 A4	29/11/2000
		EP 1023582 B1	19/11/2003
		EP 1265063 A1	11/12/2002
		EP 1265063 B1	26/01/2005
		EP 1508799 A2	23/02/2005
		EP 1508799 A3	18/05/2005
		EP 1508799 B1	04/02/2009
		JP 2001-516874 A	02/10/2001
		JP 2004-531735 A	14/10/2004
		JP 4001862 B2	31/10/2007
		JP 4499279 B2	07/07/2010
		US 2001-0000679 A1	03/05/2001
		US 2001-0000977 A1	10/05/2001
		US 2001-0002149 A1	31/05/2001
		US 2001-0052975 A1	20/12/2001
		US 2002-0080346 A1	27/06/2002
		US 2003-0206295 A1	06/11/2003
		US 2004-0057045 A1	25/03/2004
		US 2005-0099621 A1	12/05/2005
		US 2005-0134841 A1	23/06/2005
		US 2005-0174568 A1	11/08/2005
		US 2005-0206886 A1	22/09/2005
		US 2006-0007435 A1	12/01/2006
		US 6384910 B2	07/05/2002
		US 6618134 B2	09/09/2003
		US 6639662 B2	28/10/2003
		US 6657715 B2	02/12/2003

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/US2014/032579**

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		US 6891611 B1	10/05/2005
		US 6956644 B2	18/10/2005
		US 7064821 B2	20/06/2006
		US 7079238 B2	18/07/2006
		US 7119897 B2	10/10/2006
		US 7218392 B2	15/05/2007
		WO 03-001186 A1	03/01/2003
		WO 99-14575 A1	25/03/1999
		WO 99-14575 B1	03/06/1999
JP 2004-031452 A	29/01/2004	JP 4165129 B2	15/10/2008
US 05146296 A	08/09/1992	US 5021854 A	04/06/1991
		US 5146296 A	08/09/1992