

Coatings for sensing and protection in silicon sensors

PJ French*

EI-EWI, TU Delft, Mekelweg 4, 2628CD, Delft, The Netherlands

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Abstract

Silicon is an excellent material for sensing. Sensors for all signal domains can be realised, and in many cases, integrated with read-out electronics. However, in some applications an addition layer may be required for sensing and/or to protect the silicon device. Piezoelectric, polymers or magneto resistive layers can be added to expand the options of silicon. In the case of some implants, the polymer is used to protect the body from the device. In harsh chemical environments, the coating layer can be used to protect the silicon and in some cases also function as the sensor. Layers such as SiC represent a chemically resilient layer to protect the layers below, but this layer can also be used as a sensing layer. Atomic layer deposition (ALD) provides thin uniform, and pinhole free layers which can be used as protection and sensing. Other materials include graphene. In cases such as extreme temperature, it is more difficult to protect the silicon device, and in these cases the electronics must be isolated from the heat. This paper will show examples of how coating layers can enhance the sensing capabilities of silicon devices and also provide protection. Copyright © 2018 VBRI Press.

Keywords: Silicon sensor, coatings, harsh environments.

Introduction

Since the 1960s silicon has been an important material for sensors. The ability to integrate with electronics led to the “smart sensor”. Silicon displays many physical effects which cover all signal domains. However, some effects, such as the piezoelectric effect or magneto resistive effect are not found in silicon. Piezoelectric layers can be used for both sensors and actuators. The addition of these materials can therefore enhance the sensor possibilities. As long as the processes are compatible, these materials can be incorporated in smart sensors. Piezoelectric materials include ZnO [1-2], AlN [3-4], a range of polymers, such as pvdf [5-6] and ceramics, such as PZT [7-9]. Polymers have the advantage of being a low temperature process which can easily be spun, screen printed, or inkjet printed [10-12] onto a silicon substrate. Ceramic piezoelectric layers can also be screen printed on the substrates, but these require a higher firing temperature.

Piezoelectric materials are widely used for applications such as pumping [13-14] and energy harvesting [15-16].

Within the group of magneto-resistivity there are anisotropic magnetoresistivity and giant magneto-resistivity [17-19]. Giant magneto-resistivity can be achieved by stacking extremely thin layers, which are usually deposited using MBE [20].

Other layers, such as polymers, can be used as layers for fluorescence devices [21]. An example of this

approach is an oxygen sensor using fluorescence quenching for tissue and blood measurement [22].

In many harsh environments coating layers may be used to protect the device, whether it be a sensor or simply electronics. These layers are generally used for protecting against harsh chemical environments, or damaging radiation levels. SiC is an excellent protection layer for harsh chemical environments [23]. It can also be used as a sensing layer. Atomic layer deposition (ALD) is a technique for depositing a wide range of layers [24]. The advantage of this technique is that very uniform, pinhole-free layers.

Other materials include graphene [25]. Graphene, deposited on silicon presents many sensing opportunities, also in harsh environments. The development of CVD systems has also greatly expanded the possibilities [26]. These layers can be extremely effective in protecting against harsh chemical environments. Devices can also be protected from radiation through coating or in some cases through design. In cases such as extreme temperature, it is more difficult to protect the silicon device. This paper will show how coating layers can enhance the sensing capabilities of silicon devices and also provide protection. There will also be a description of applications.

Processing

This section will describe the materials and the processing of the required materials. These include low temperature process, such as spin-coating and printing and higher temperature processes such as CVD.

Spinning & inkjet printing

These techniques are widely used for polymer based materials [27-28]. Spin coating yields a uniform layer and will also planarize the surface. The thickness of the final layer is related, d , to the spin speed, ω , by;

$$t \propto \frac{1}{\sqrt{\omega}}$$

Spin time is usually around 30 secs to 1 minute, depending on the material. A typical thickness curve as a function of spin speed is given in Fig. 1.

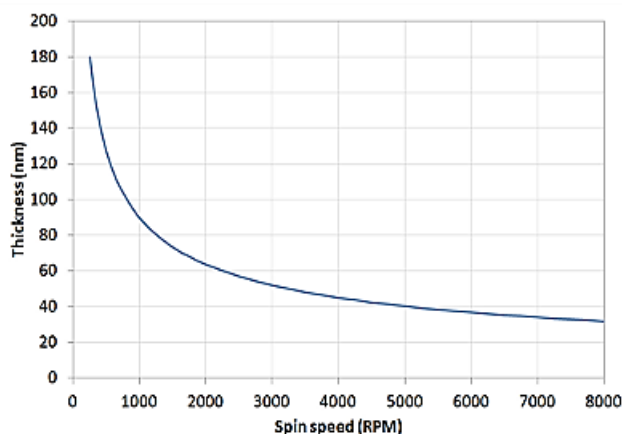


Fig. 1. Example of film thickness as a function of spin speed [29]. Courtesy of Ossila Limited's spin coating guide.

In addition to spinning on the material, this technique can be used to deposit particle in a fluidic carrier, as shown in Fig. 2.

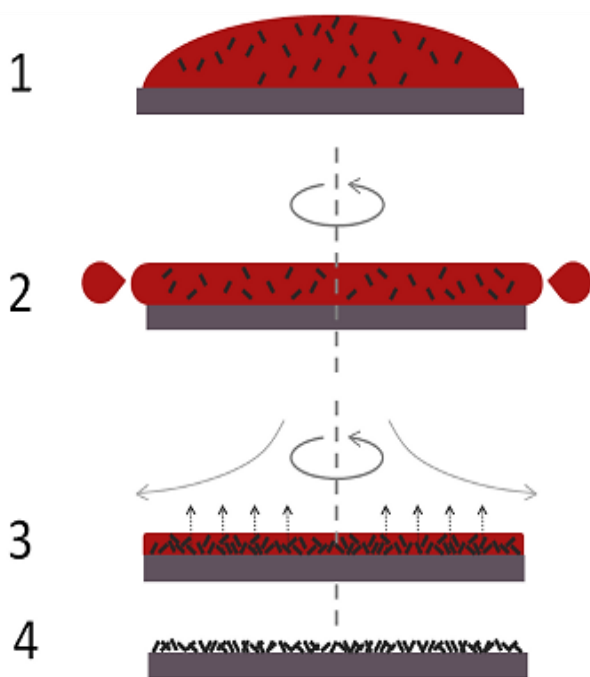


Fig. 2. Depositing particle using spin technique [29]. Courtesy of Ossila Limited's spin coating guide.

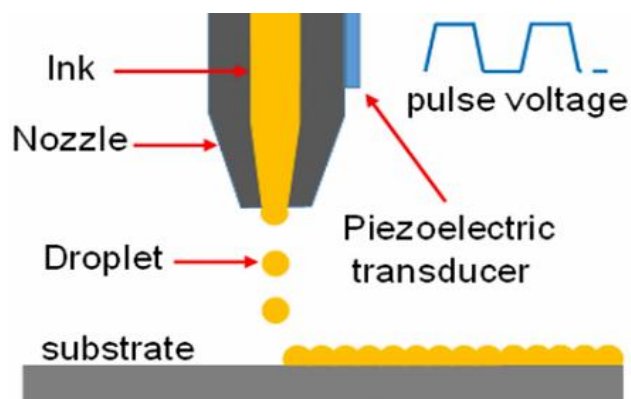


Fig. 3. Illustration of a piezoelectric driven inkjet system. Adapted from [30].

In recent years there has been increasing interest in inkjet printing for a range of materials including polymers for coating and organic electronic devices. The basic structure of such a device is given Fig. 3.

Screen printing

Screen printing, in a recognisable form, can be traced back more than 1000 years in China [31]. The basic process is shown in Fig. 4.

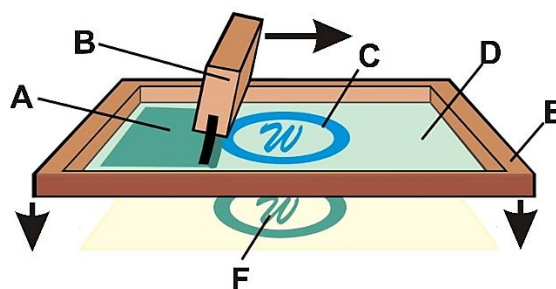


Fig. 4. Basic structure of a screen printing system A. Ink. B. Squeegee. C. Image. D. Photo-emulsion. E. Screen. F. [32].

This technique is widely used for materials such as polymers and ceramics. The main difference is that ceramics need a much higher temperature for the post deposition anneal, usually around 900C. This can be used on wafers, or on rolls of material.

Chemical vapour deposition (CVD)

The main forms of CVD are low pressure CVD (LPCVD), atmospheric pressure CVD (APCVD) and plasma enhanced CVD (PECVD). The use of plasma in PECVD greatly reduces the deposition temperature (usually below 400C), making it suitable for use on fully processed CMOS wafers. In standard processing, CVD is used for materials such as SiO₂, SiN and polysilicon. Other materials of interest for coating on silicon include SiC and graphene. The basis of all these processes is to choose gasses which break down in the chamber to deposit the required material. For example, polysilicon is usually deposited using SiH₄, which breaks down into Si + 2H₂.

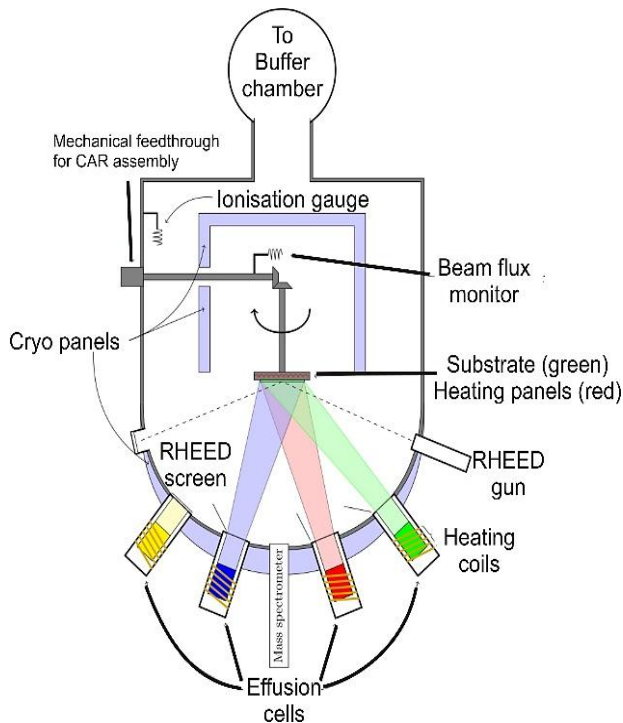


Fig. 5. Illustration of the main structure of a MBE system [34].

Molecular beam epitaxy (MBE)

MBE was invented in the 1960s at Bell Telephone Laboratories by JR Arthur and AY Cho [33]. The process takes place at high or ultra-high vacuum, typically (10^{-8} - 10^{-12}). This technique, shown in Fig. 5 is widely used for compound semiconductors, such as GaAs. It can also be used for deposition of multi-layers.

Atomic layer deposition (ALD)

As the name suggests, this is a technique to deposit layers at atomic level. Since the deposition is layer-by-layer at atomic level, the layers are extremely uniform and pinhole free [35-36]. It was developed in the 1960s by Prof. Kol'tsov from Leningrad Technological Institute, although the basic concept was proposed by Prof. Aleskovski in his PhD thesis in 1952. The important difference of ALD from other deposition techniques is self-limiting chemisorption of precursors in each half-cycle [36].

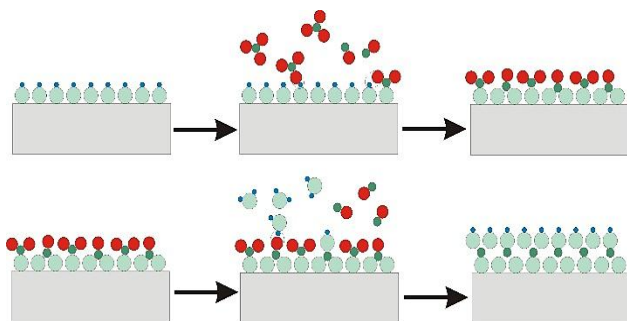


Fig. 6. Illustration of the cycling of the ALD process [37].

Sputtering & evaporation

These techniques are widely used for metals, although other materials are also deposited this way. With sputtering the ions are accelerated towards the substrate. The basic principle is illustrated in Fig. 7.

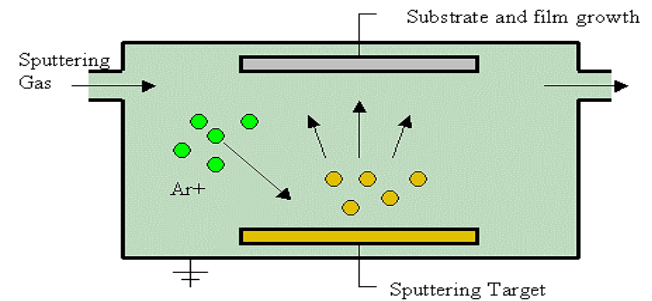


Fig. 7. Basic principle of the sputtering technique [38].

Evaporation systems use high vacuum to allow vapour of the required material to deposit on the substrate. There are a number of configurations, and one example, from Hivatec is given in Fig. 8.

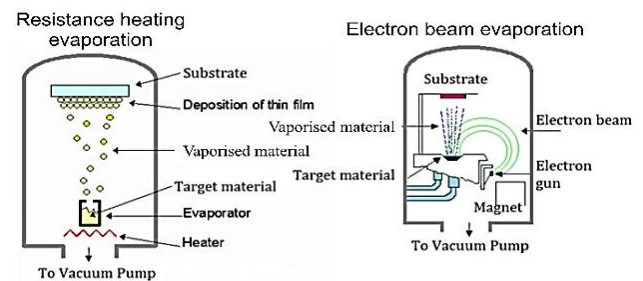


Fig. 8. Examples of evaporation systems [39].

Materials

There is a wide range of materials which can be combined with silicon as a protection layer or to expand functionality. In standard IC processing, layers such as SiO₂ and SiN are widely used as surface passivation and insulation. Additional materials such as SiC can be used as a sensing layer and also a protection layer.

Protection layer

The main use for protection layer is for harsh chemical environments. For this SiC is an excellent choice it can be deposited using PECVD and is thus a suitable layer for coating processed IC devices [40]. This layer is extremely chemically resistant [41].

For medical implants the coating layers serve to protect the silicon device from this harsh environment, and also to achieve biocompatibility. For this, there are a number of materials. A wide range of polymers are available for this application. Polymers are composed of a large, chain-like molecular structure made of monomers, which are covalently linked in 3D networks. These layers can be used as coating and also sensing. There are both

natural and synthetic polymers [42]. As a protection layer, many are biocompatible and able to protect the device underneath. Examples of these polymers include the following:

- Natural
 - Plants: Cellulose, natural rubber
 - Animals: Collagen, heparin, DNA
- Synthetic
 - Parylene
 - Silicone rubber
 - Polyethylene (PE)
 - Polypropylene (PP)
 - Poly methyl methacrylate (PMMA)
 - Poly vinyl chloride (PVC)
 - Polyether ether ketone (PEEK)

Materials such as Parylene [43-48] and silicone rubber [49-50] are widely used as coating layers for medical implants.

Sensing and actuating layers

Although silicon is an excellent sensing material for many applications, there are some effects not found in silicon and in some cases additional layers are required to generate a reaction, such as in bio-chemical sensors.

The main effects not found in silicon are the piezoelectric effect and the magnetoresistive effect, although there are other effects found in silicon.

The piezoelectric effect transforms the mechanical signal directly into a voltage, and also a voltage into mechanical deflection. There are a number of materials which are suitable for integration with silicon. Frequently used materials include ZnO, AlN and a range of polymers. Other materials are quartz and GaAs. Both ZnO and AlN are usually deposited using sputtering [51-52] or CVD [53-54]. Quartz is usually bonded to silicon rather than being deposited, whereas GaAs is usually formed using techniques such as MBE.

The magnetoresistive effect is the change of resistivity of a material as a function of magnetic field. This was first discovered by Thomson in 1851, and can be divided into a number of forms: anisotropic [55], giant [56], colossal [57] and tunnelling [58]. In addition to integration with silicon, there are examples of GMR devices being formed on flexible substrates [59]. There are also many examples of integration of magnetoresistive layers with silicon [60-63]. Devices for anisotropic magnetoresistance use permalloys such as Ni-Fe. The giant magnetoresistive effect is found in multi-layers of alternating ferromagnetic and non-ferromagnetic conductive layers. This became possible when techniques were developed for depositing extremely thin and uniform layers. This development became extremely important in the massive increase in hard-disc capacity. The basic structure is shown in Fig. 9. Commonly used layers include Fe-Cr [64].



Fig. 9. Basic structure of a giant magnetoresistive device.

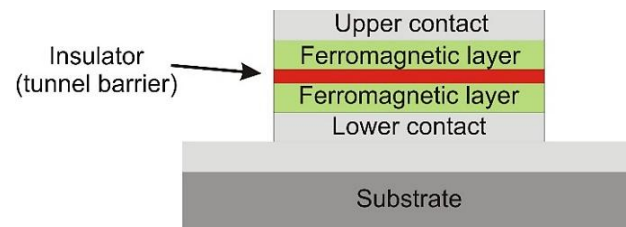


Fig. 10. Basic structure of a tunnelling magnetoresistive device [65].

Colossal magnetoresistive devices usually is manganese-based perovskite oxides. The tunnel effect also requires the ability to deposit layers of a few nm, but the structure is quite different, as shown in Fig. 10.

Fluorescent devices mainly use materials such as polymers or hydrogels, which are either exposed directly to the environment, or covered with a membrane which allows the element of interest through. Examples of these devices, will be given in the next section.

Applications

Piezoelectric devices

As mentioned above, the piezoelectric effect can be used for both sensors & actuators. In the field of actuators, piezoelectric layers are commonly used for pumps, grippers and motors, etc. Although piezoelectric grippers and motors are not usually integrated into silicon. Micropumps use pressure differences to pull the fluid through, there are a number of actuation techniques, such as thermal, magnetic and electrostatic. Piezoelectric pumps [66-68] have a relatively simple structure needing only a piezoelectric layer on a membrane. The basic operation can be seen in Fig. 11.

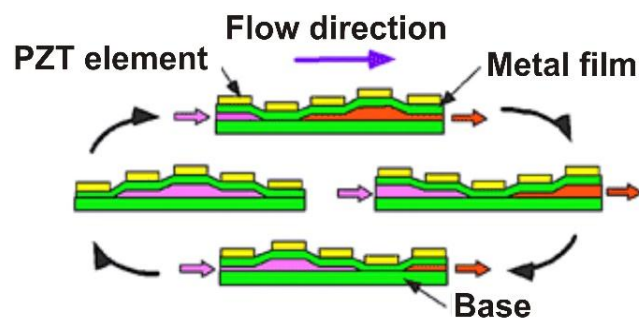


Fig. 11. Basic operation of a piezoelectric micropump. From Yoshida & Kim lab, Tokyo Institute of Technology, Japan [69].

In the field of sensors there are many examples of piezoelectric materials being integrated in silicon. One type of device which uses both the actuating and sensing properties of the piezoelectric material is the surface acoustic wave device [70-73]. The basic principle of the device (shown in Fig. 12) is to generate an acoustic wave using finger type electrodes. The wave passes along the surface of the device and is detected by a second set of electrodes. If, for example, the wave passes along a membrane, the speed of the wave can be modulated if the membrane comes into contact with a fluid. It is further dependent on the density and viscosity of the fluid. Using a reference path and a feedback, a frequency difference, as a function of the desired parameter can be produced. This basic structure is given in Fig.12.

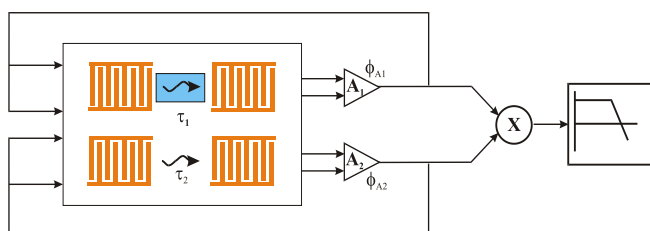


Fig. 12. Basic SAW device.

The same basic principle can be used for a number of other parameters. Piezoelectric layers can also be used for measuring strain directly. Piezoelectric materials have also been used as actuation and sensing in gyroscopes. In other cases, the piezoelectric layer is used for actuation and another method used for sensing [74].

Magnetic sensors

Provided the magnetoresistive material can be deposited on silicon, at a relatively low temperature, it is possible to fabricate integrated magnetoresistive devices. In many cases, these resistors are formed in a Wheatstone bridge, as often used in mechanical devices. An example of this basic structure is shown in Fig. 13.

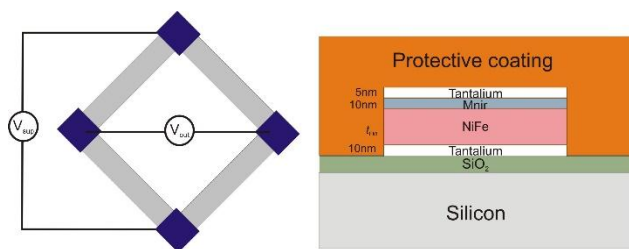


Fig. 13. Illustration of the sensor geometry and the sensor stack with definitions of geometrical and electrical parameters [75].

Bio-chemical sensors

Many chemical sensors require an additional layer to react with, or trap the element of interest. An early example of this was the ChemFET. First proposed by Prof. Piet Bergveld, in The Netherlands, this uses a standard MOSFET structure, but replaces the gate with a material

which traps or reacts with the chemical or biological element [76]. From this first idea, a wide range of chemical and biological sensors have been developed.

Optical devices, such as waveguides can also be used when additional layers are added to trap elements. One such example (Fig. 14), uses the evanescent wave along a thin waveguide. If the waveguide surface is coated with a layer to trap, in this case, a bacterium, the absorption of light, will increase with increasing presence of the bacteria. Therefore, the intensity of the out coming light will be reduced. The example given in Fig. 14 uses a TiO₂ waveguide. Similar structures have been made using materials such as SiC and SU8 [79]. All these devices were fabricated using a silicon substrate.

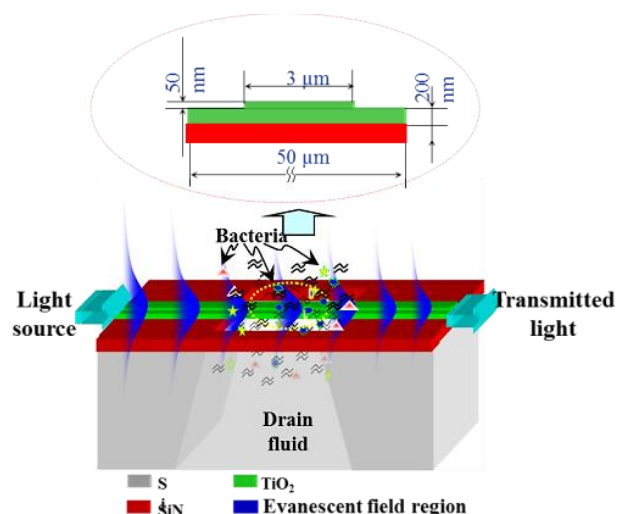


Fig. 14. Waveguide bacteria sensor using the evanescent wave [78].

Fluorescent techniques are also commonly used in chemical and biochemical devices. They require an additional layer, often polymer or hydrogel, which has been modified to fluoresce when in the presence of the compound of interest. One such example is to measure oxygen using fluorescence quenching. A porous polymer impregnated with ruthenium is used. When illuminated with blue light, it fluoresces with red. If oxygen enters the polymer, the fluorescence will be quenched. The more oxygen present, the faster the quenching. Measuring the speed of the quenching gives us the partial pressure of oxygen. This can be used to measure oxygen in tissue, blood and gasses [22]. For measuring CO₂, HPTS-(TOA)₃ can be added, although this is an intensity measurement and not fluorescence quenching [79]. These two sensors can be combined to make a tissue viability sensor. They can also be integrated into a silicon device using a single activating light source. The basic structure is given in Fig. 15.

Another example is a glucose sensor using a hydrogel. The device, shown in Fig. 16, using a membrane allowing glucose to pass through to reach a glucose responsive fluorescent hydrogel. The whole device can be implanted under the skin and uses wireless connection to a hand-held device. Ammonia is aggressive

to many materials, including silicon. In this application, SiC can serve as a protection layer, and also a sensing layer. Porous silicon carbide can be made to be sensitive to both humidity and ammonia depending on the structure of the pores [23].

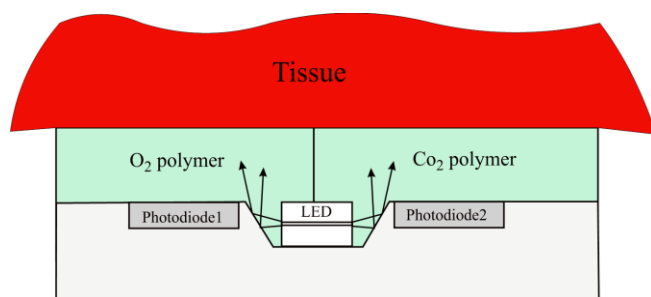


Fig. 15. Cross-section of an O₂-CO₂ tissue vitality sensor.

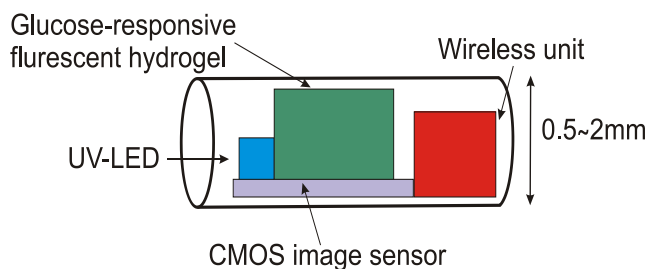


Fig. 16. Glucose sensor using a hydrogel on top of a CMOS image sensor. Adapted from [80].

SiC can be deposited over the whole wafer, using PECVD and only made porous in the sensor area. This is achieved since the formation of porous SiC is an electrochemical process and is only formed above the bottom electrode. This way, it serves as both protection and sensor. The basic structure is shown in Fig. 17.

Graphene is also a material which is robust and can be deposited on silicon. Since the development of CVD systems for graphene, the possibilities for integration have become greater [81]. Just as in SiC, graphene can be used for humidity and gas sensing and a range of chemical sensors [82-85].

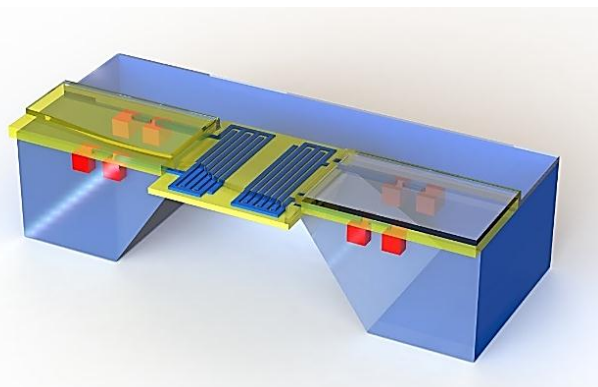


Fig. 17. Ammonia/humidity sensor using porous SiC as sensor and SiC as protection layer.

Conclusions

Silicon is an excellent material for electronics and a wide range of sensors. However, in many applications we require additional functionality, or additional protection from the environment. Additional layers can be used to make piezoelectric or magnetoresistive layers. They can also be used to react with the environment to generate fluorescence, change colour, or increase optical absorption. As a protective layer material such as SiC serve as an excellent chemical protection for the surface of the silicon. In medical implants, it is important not only to protect the silicon from this harsh environment, but also to ensure no adverse reaction from the surrounding tissue. For this material such as polyene, polymers and silicone are often used. This combination of silicon with additional layers can greatly expand the options for silicon sensors and smart sensors.

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