Review

Sensitive Materials and Coating Technologies for Surface Acoustic Wave Sensors

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Abstract: Since their development, surface acoustic wave (SAW) devices have attracted much research attention due to their unique functional characteristics, which make them appropriate for the detection of chemical species. The scientific community has directed its efforts toward the development and integration of new materials as sensing elements in SAW sensor technology with a large area of applications, such as for example the detection of volatile organic compounds, warfare chemicals, or food spoilage, just to name a few. Thin films play an important role and are essential as recognition elements in sensor structures due to their wide range of capabilities. In addition, other requisites are the development and application of new thin film deposition techniques as well as the possibility to tune the size and properties of the materials. This review article surveys the latest progress in engineered complex materials, i.e., polymers or functionalized carbonaceous materials, for applications as recognizing elements in miniaturized SAW sensors. It starts with an overview of chemoselective polymers and the synthesis of functionalized carbon nanotubes and graphene, which is followed by surveys of various coating technologies and routes for SAW sensors. Different coating techniques for SAW sensors are highlighted, which provides new approaches and perspective to meet the challenges of sensitive and selective gas sensing.

Keywords: SAW; chemoselective polymers; CNT; carbon; LIFT; laser

1. Introduction

Ever since the 1970s, air pollution has become a constant concern for most governments around the world. Even though in recent years, air quality in Europe has improved, the levels of volatile organic compounds in air still exceed most World Health Organization standards. In addition, the possibility of attacks using explosives and biological or chemical weapons is a major issue for public security.

Therefore, there is a great need for countermeasures, in particular for innovative and efficient detection solutions i.e., technologies, equipment, procedures, etc. Key requirements include, and are not limited to, the determination of the minimum allowed amount of compounds, the possibility to discriminate the compounds of interest from background interferents such as water, and the costs associated with the solution provided.

Currently, there is a large number of techniques and state-of-the-art equipment available for the precise monitoring of trace levels of dangerous compounds such as volatile organic (VOC) compounds, explosives and precursors, or biological or chemical agents in complex mixtures.

Current detection technologies rely either on point or standoff detectors, and while standoff detectors are based on infrared remote sensing techniques, point detectors are based on methods such as colorimetry, ion mobility spectrometry, flame photometry,
mass spectrometry, electrochemistry, enzyme or immunoassay approaches, and surface acoustic wave (SAW) sensors. However, since the topic of this review is centered around surface acoustic wave sensors, we will only briefly present a few of the point and standoff detection techniques.

For example, infrared or Raman vibrational spectroscopies are analytical techniques widely used for the detection and identification of chemical agents, with the possibility to be used remotely. Infrared spectroscopy (IR) relies on IR light absorption and scattering to different degrees at various wavelengths of the substances of interest. An IR spectrometer shines light into a sample and quantifies the light returned over a wide range of optical wavelengths. Absorbance is due to the loss of IR light following its interaction with CH, OH, NH, and other molecular bonds, whose vibrational frequencies are identical to the frequency of the incoming light. By IR spectroscopy, different substances can be measured, for example octane in gasoline, alcohol content in beverages, or the composition of drugs.

A technique similar to IR spectroscopy, i.e., Raman spectroscopy, is widely used due to its ability to distinguish between molecules that have a high degree of symmetry.

Furthermore, colorimetric sensors [1,2] are used to determine chemical agents in terms of color changes. The most common use of colorimetric detectors is pH paper (litmus paper), which is meant to test the pH of a solution and the water test kit for the determination of the chlorine concentration in swimming pools [3]. Colorimetric detectors are easy to use, low cost, and offer fast responses [4,5]. However, this method has the disadvantage of requiring many sensors for multiple field applications.

Electrochemical sensors use a working electrode to measure either the conductivity, potential, or current changes, and depending on their working principle, they can be classified into solution-phase or solid-phase electrochemical sensors [6].

Ion mobility spectrometry (IMS) technology is used for the on-site detection of trace quantities of chemicals. IMS is based on time-of-flight principles, and it measures the small differences in the velocity of ions along a cylindrical tube, across which a constant electric field is applied. IMS instruments are frequently used in airports to detect explosives and narcotics [7].

Gas and liquid chromatographic systems are portable and reliable; however, their sensitivities are not high enough to detect ultra-low concentrations. Therefore, gas chromatography was combined with mass spectrometry to detect specific chemical warfare agents, precursors, or degradation products. Although the two combined techniques become sensitive, they require long processing times, careful liquid handling, and expensive reagents and apparatus [8].

Another detection technology, i.e., flame photometry, allows for the detection of phosphorus and sulfur by analyzing the color of an air-sample, burnt with a hydrogen flame, by a photometer [9].

Furthermore, biological methods such as immunoassay and inhibition studies, e.g., monitoring of the acetylcholinesterase activity, show a great potential for the detection of chemical warfare agents for example; however, they suffer from extensive sample handling procedures and are at present not suitable for real-time monitoring [10,11].

Almost all of the conventional detection systems presented above have drawbacks and limitations either due to the high cost of the analytical systems or their unavailability. Therefore, it is essential to develop novel devices that simultaneously provide the fast detection and quantification of the volatile organic species or other dangerous compounds that are easy to use and cost effective.

The increasing demand of sensor devices in applications ranging from electronics and telecommunications to the biomedical area has prompted the rapid development of electro-acoustic devices for high-frequency applications.

Acoustic sensors and biosensors are promising solutions for the fast, sensitive, and low-cost detection of gaseous and liquid analytes. The most common acoustic sensors are based either on bulk or surface acoustic waves, and a scheme of the different types of acoustic sensors and their operation frequencies is shown in Figure 1.
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Detailed overviews of the fundamentals of bulk acoustic waves and their characteristics are thoroughly reviewed in [12–15].

Generally, both types of acoustic sensors rely on the piezoelectric and the inverse piezoelectric effect; i.e., they are based on piezoelectric materials that produce an electrical potential when subjected to mechanical stress and vice versa, producing an internal mechanical stress when an electrical potential is applied.

Briefly, the quartz crystal microbalances (QCMs), also known as quartz microbalances (QMBs), are small plates of quartz; generally, these have an AT cut that offers the advantage of a minimal temperature effect on the resonance frequency at 25 °C operation temperature. Since the first report of King et al. [16] on the development of humidity/vapor gas sensors, numerous QCM sensors have been reported for both gas and liquid sensing, including biosensing applications. Although QCMs are the most studied acoustic sensors, their limitations are linked to their operating frequencies and higher operation frequencies that result in higher mass sensitivities are desired.

In addition, the thin film bulk acoustic resonators (TFBARs) consist of a resonator film (for example an aluminum nitride or zinc oxide film), which is solidly mounted on a support structure. Depending on the device configuration, the TFBARs can be divided into back trench, Bragg acoustic mirror, or air-bag type, and they can be operated in longitudinal mode or in thickness shear mode (preferred in liquids to minimize energy loss) [14].

Piezoelectric-based SAW devices consist of two metallic interdigital transducers (IDTs) that are designed as a delay line structure and are implemented onto a piezoelectric substrate, as illustrated in Figure 2a. They were first developed by White and Voltmer [17] in 1965.

The SAW resonators may be either 1-port or 2-port devices having acoustic reflective electrode gratings that create a resonant cavity. While the single port is used both for the input and output for the 1-port devices, the 2-port devices have separate input and output ports [18]. A scheme of a 2-port resonator is shown in Figure 2b.

The operating principle of the 2-port SAW resonators is simple, and it is based on applying an alternating voltage to the input IDT, leading to the electrodes becoming alternatively positively or negatively charged, thus creating an electric field between them. The field distribution induces strain in the piezoelectric substrate, resulting in the formation of surface acoustic waves. The acoustic waves travel along the surface to the output IDT, where the acoustic wave energy is converted into an electrical signal. The Rayleigh mode, named after its discoverer Lord Rayleigh, is the most commonly encountered wave propagation mode for SAW-based gas sensors [18].
The first Rayleigh-mode surface acoustic wave device was reported by Wohltjen and Dessy in [19–21]. The authors coated the device with a sensitive polymer layer and used it to detect gaseous organic compounds [19–21]. Since then, a large number of SAW devices have been developed for applications in gas and liquid sensing [22,23].

In this work, the present coating technologies for surface acoustic wave devices and the new opportunities of ”soft” sensor materials are reviewed.

2. Active Materials in SAW Sensors

Owing to the fast developments in the fields of materials science, nanotechnology, biology, and chemistry, a large variety of natural occurring substances (such as cells, enzymes, receptors, and antibodies) are ordinarily used as chemical interactive membranes (CIM) in sensor technology.

Moreover, due to the requirements for implementation into acoustic wave devices, i.e., ease of processing, compatibility with the transducer, physical and chemical stability, and good sensitivity toward analytes, just to name a few, a large range of materials have been evaluated, from pristine polymers to biocompounds such as DNA, proteins, or peptides. A scheme of the materials used as active sensing coatings in SAW devices is shown in Figure 3.

Figure 2. Schematic representation of (a) a SAW delay line and (b) a 2-port SAW resonator coated by an active sensing layer.

Figure 3. Scheme of the materials used as active sensing coatings in SAW devices.
Few examples of active materials applied as sensing layers in SAW devices include polymers and hybrid materials based on polymers [24–27], molecularly imprinted polymers [28,29], supramolecular structures [30], self-assembled monolayers [31,32], nanosstructured metal oxides [33–35], carbon nanotubes [36,37], or functionalized and/or the mixtures of two or more recognition materials [38].

A few of these materials will be briefly introduced below. In this work, the focus is on the new opportunities of “soft” sensor materials, i.e., pristine polymers together with carbonaceous materials such as carbon nanotubes and graphene/graphene oxide.

Molecularly imprinted polymers (MIPs) are materials specifically designed to resemble the biological systems from which they were inspired, thus providing high selectivity [39–41]. Briefly, MIPs are prepared by adding a template in the polymerization process of monomers, which is removed after polymer synthesis. Although MIPs have a wide range of advantages, such as chemical and mechanical stability, specificity toward target molecules, and low cost, they also present disadvantages, i.e., large size, rigid, and insoluble, which limit their usage in SAW devices.

Other active coating materials include self-assembled monolayers and their derivatives, such as cavitand receptor materials, which offer the possibility to catch foreign atoms with appropriate size and chemical properties [42]. A few examples include porphyrins [43], metal-free phthalocyanines [44], calixarenes [45], or corroles [30].

Another class of materials used as CIMs in SAW sensors is the group of uniform materials based on organic salts (in short, GUMBOS). These materials rely on phthalocyanines and porphyrins, and they have been demonstrated for the detection of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, acetone, chloroform, toluene, etc. [46].

Last, biocompounds such as DNA, peptides, and proteins are more and more used in SAW biosensors for different applications ranging from the biomedical to the biotechnological fields. For example, SAW biosensors based on antibodies or single-stranded DNA have been reported for the detection of antigens or the corresponding DNA strands [22,47–49].

2.1. Pristine Polymer Sensing Layers in SAW Sensors

Polymers are most frequently used as active layers in sensor devices due to their large range of capabilities. Therefore, here, we will give some examples of polymer active layers in SAW sensors [50].

Since the first reports on polymeric sensor materials in the 1960s [51–53], and given the extensive research undertaken in micro and nano-scale fabrication methods, characterization techniques, and molecular interactions, state-of-the-art sensing concepts have been successfully demonstrated and validated [54].

Even more, as nowadays polymers are readily available and easily tunable in terms of functional groups present in/on polymeric backbone, they can be used for the detection of different analyte vapors [55–60].

The first examples of polymers applied in bioanalytical sensors as sensitive elements are conductive polymers such as polypyrroles (PPy) and polyanilines (PANI). PPy and PANi are very promising for the detection of volatile organic compounds (VOCs) at room temperature, because they can be easily synthesized at low costs, and they are frequently used for odor detection and identification [61–64].

In addition, poly(pyrrrole) (PPy)–bromophenol blue (BPB) layers have been successfully used as sensing layers toward several analytes including TNT (trinitrotoluene), [3-nitrooxy-2,2-bis (nitrooxymethyl)propyl] nitrate (PETN), 1,3,5-trinitroperhydro1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) [65]. The authors reported very low limit of detections for nitroexplosives, i.e., 500 and 800 ppb for TNT and PETN, respectively, and 1 and 2 ppb for RDX and HMX, respectively.

In [66], several polymers are presented, which have been used to detect nitroaromatic explosives, such as TNT. The polymers are polycetylenes and poly(p-phenylenethylenes), which are strongly luminescent conjugated polymers with high permeabilities to small molecule analytes, such as nitroaromatics. Other polymers proposed in this study to detect
nitroaromatic explosives [66] are poly(p-phenyleneethynylenes), polymeric porphyrins, and polysilanes. Different siloxane polymers functionalized with acidic groups are the most promising materials for nitroaromatic compounds detection, as reported in [67]. The detection limit for 2,4-dinitro-toluene vapor with a 250-MHz SAW device, coated with the polymer SXPHFA, is approximately 235 ppt [67].

Other polymers that present interesting properties for sensing applications are chemoselective polymers, such as polyisobutylene (PIB), polyepichlorhydrine (PECH), and polyethylenimine (PEI).

The detection of the target molecule with such polymers relies on their ability to form weak hydrogen bonds with the analyte molecules. Generally, the functional polymer group may be a hydroxyl (OH) or a NH$_2$ bond and a hydrophobic group (for example a fluorinated (CF$_n$) or siloxanes groups –Si–C–O–Si– or –Si–O–Si–C). The polar nature of the hydroxyl unit attracts a single oxygen atom within the target analyte molecule, and a weak hydrogen bond is thus formed [54]. Moreover, these polymers are cheap, present low toxicity, and no special care is required when handling them.

PECH is an interesting polymer given the presence of reactive chlorine groups on its backbone, which result in nucleophilic substitution for side-chain modifications [68]. Thus, PECH has a high capacity for DMMP and toluene absorption [69–71]. For example, Di Pietrantonio et al. used laser-induced forward transfer to deposit PECH on Q-SAW, and good sensitivities of 649 Hz/ppmV toward DMMP and 150 ppbv detection limit have been reported [72,73].

PEI has numerous applications, ranging from chemical sensing, due to its reactivity with hydrazine-based compounds, to the biomedical field, due to its capability as a transfection enhancer [74,75]. The monomer consists of a three-membered ring with two -CH$_2$- linkages and a secondary amine group, =NH.

PIB is a vinyl polymer with a structure similar to that of polypropylene, having two methyl groups substituted on every other carbon atom. It has excellent impermeability and high flexibility. PIB is largely utilized in sensor applications, in chemiresistors, chemicapacitors, microcantilever, and optical sensors. PIB is a strong hydrogen-bond acidic polymer, and it presents a high sensitivity to organophosphorus nerve agents [76–81]. One of the early works on chemoselective polymers for SAW sensors is the work of McGill et al. whom reported an e-nose ("NRL-SAWRHINO") based on SAW sensors coated with functionalized polymers for CWA [79]. The authors of the work could show that the discrimination and clustering in the first two principal components of the nerve and blister chemical agents, in the presence of different interferents, was error free.

Quantitative characteristics for some of the most representative polymer active layers are summarized in Table 1.
Table 1. Quantitative characteristics for SAW sensors based on different polymer active coatings.

| Sensitive Layer                  | Sensor Type | Target Analytes | Sensitivity       | Detection Limit            | Remarks                                                | Ref. |
|----------------------------------|-------------|-----------------|-------------------|----------------------------|--------------------------------------------------------|------|
| polypyrrole                      | SAW         | NH$_3$          | -                 | -                          | Interferents: (CO, CH$_4$, H$_2$, O$_2$) Good response time to NH$_3$ | [63] |
| polypyrrole                      | SAW         | glyphosate      | (6.9 ± 2.9) × 10$^{-20}$/nM | 1 pM                      | -                                                      |      |
| polypropylene-bromophenol blue   | Q-TSMR      | Nitroaromatic compounds (TNT, PETN, RDX, HMX) | - | 500 ppt for TNT; 800 ppt for PETN; 1 ppb for RDX; 2 ppb for HMX | Selectivity toward TNT | [64] |
| HFIP functionalized siloxane polymers | SAW/250 MHz | Nitroaromatic compounds | - | 235 ppt | - | | [65] |
| poly(siloxanes), PECH            | Q-SAW (ST)  | Warfare agents simulants | - | - | classification | [71] |
| PIB, PECH, PEI                   | Q-SAW/392 MHz | sarin DMMP | 600 Hz/ppm | 15.41 × 10$^{-3}$ ppm | Best values for PECH, followed by PEI, and PIB | [72] |
| PIB, PECH, PEI, PScMA-me, HPMC   | Q-SAW/392 MHz | EtOAc, DCM, DMMP, H$_2$O, DCP | 86 Hz/ppm | 0.3 ppm | Best values for PECH; Good discrimination; | [73] |
| chemoselective polymers          | Q-SAW/250 kHz | CWA | - | GB = 4 ppb/mustard = 80 ppb | - | | [73] |
| chemoselective polymers (PIB, PECH, PDMS, PIP, PBD) | Q-SAW/264 MHz | CWA/DMMP, acetonitrile, DCM, DCP | - | - | Good discrimination | [69] |
| poly (3-hexyl thiophene)         | QCM         | VOCs            | -                 | 1.5                        | LDL = 3% permissible exposure limit 180/120 sec response and recovery times | [80] |
| poly(siloxanes), PEI, PECH, Carbowax | Q-LOWE SAW  | DMMMP and CWA | 40,200 Hz/ppmv | 40 ppbv | Principal component 2 = 1% variance Good discrimination | [77] |
| polymer array (PBMA, PIB, PDMS, PCFV, PECH, silar, L grease, polyurethane alkyd resin with trace isocyanates) | STW         | VOC             | -                 | -                          | - Polar plots | [81] |

Legend: SAW = surface acoustic wave; Q-TSMR = quartz-thickness shear mode resonator; NH$_3$ = ammonia; TNT = trinitrotoluene, PETN = [3-nitrooxy-2,2-bis (nitrooxymethyl) propyl] nitrate; RDX = 1,3,5-trinitrohexahydro-1,3,5-triazine; HMX = octahydro-1,3,5,7-tetrinitro-1,3,5,7-tetrazocine; HFIP = hexafluorisopropanol groups; PECH = poly(epichlorhydrin); PIB = polyisobutylene; PEI = polyethylene imine; HPMC = (hydroxypropyl)methyl cellulose; PScMA-me = poly(styrene-co-maleic acid) partial isobutyl/methyl mixed ester; DMMMP = dimethyl methylphosphonate; EOAc = ethyl acetate; DCM = dichloromethane; DCP = dichloropentane; PDMS = polydimethylsiloxane; PIP = polyisoprene; CWA = chemical warfare agents; GB = soman nerve agent; PBD = polybutadiene; STW = surface transverse wave resonators; PBMA = poly(butyl methacrylate); PCFV = poly(chlorotrifluoroethylene-co-vinylidene fluoride).
2.2. Carbonaceous Structures as Matrices for SAW Sensors

Among the carbon-based structures known today, the most important are carbon nanotubes and graphene. Originally used only to increase the mechanical and thermal properties of composite materials, especially polymers, due to their remarkable mechanical properties [82–86], carbon nanotubes were subsequently exploited for their electrical properties, especially in the manufacture of contactors or sensors. In order to make the best use of nanotubes in the field of sensors, computational modeling has been performed and reported to study the predictability of nanotubes behavior when interacting with species to be detected. Molecular modeling was used to predict the adsorption capacity of different single-walled carbon nanotubes (SWCNT) for gases such as SO$_2$ [87], CO$_2$ [88], NH$_3$ [89], CO [90], CH$_3$SH [91], and H$_2$CO [92]. The adsorption of NO$_2$ has also been studied by computational modeling on SWCNT doped with Pd. The data obtained showed a much higher adsorption capacity of Pd-CNT compared to CNT; at the same time, the adsorption of gas increasing the C-Pd connecting energy had an effect in stabilizing the structure of doped nanotubes [93]. In addition, by computational modeling was used to investigate the adsorption of NH$_3$, PH$_3$, and AsH$_3$ on SWCNT nanotubes doped with Sc, Ti, V, and Cr, investigating mainly the adsorption mechanism. The study showed that by replacing a C atom in the CNT structure of type 5, 5 armor, the adsorption capacity of the gases increased several dozen times, in order NH$_3$ > PH$_3$ > AsH$_3$, also depending on the doping atom, decreasing in order Cr > V > Sc > Ti [94]. In addition, the modeling study of H, O, and N adsorption on Ni-SWCNT and Fe-SWCNT, respectively, showed an increased capacity of doped nanotubes for adsorption of these gases, as well as inducing catalytic activity for subsequent gas transformation reactions, especially in the case of Ni. The study opens the possibility of designing devices with dual roles—catalyst and sensor, especially for the automotive industry [95].

From the point of view of the use of CNT for SAW structures, they have the advantage of being easily deposited from solvents in which they were dispersed; however, the question remains related to the stability of the deposited film as well as its adherence to the substrate. The initial applications were aimed at obtaining SAW sensors for gases or volatile organic substances [96].

Very good results were obtained for the manufacture of SAW sensors for gas detection, especially carbon dioxide, using amino carbon nanotubes as such or entrapped in various polymer matrices (such as polyethylene) [97–99]. Carbon nanotubes with amino groups have two advantages, both in terms of ensuring the elasticity of the composite matrix and assuring the specific interaction with the carbon dioxide molecules, with the formation of carbamates involving the easier and accurate detection of this gas. In addition to the use of nanotubes with amino groups, sensitive matrices, with equally good performance, based on polymers with amino or imine groups, such as polyaniline [100], were used. Accelerating the interaction between -NH- groups and carbon dioxide molecules provides the detection mechanism, the presence of CNT improving the conductivity and elasticity of the entire matrix. The use of CNT as such in CO$_2$ detection is also favored by the C-C interaction between gas and nano species surface [101,102]. Apart from the influence of the type of CNT used or the nature of the polymer in the case of composite matrices, it was found that an important factor is also the working frequency of the sensor, a large study showing that it is optimal at 286 MHz [103].

The sensitivity and limit of detection depend on both the detection system used and also the chemical nature (especially the molecular mass) of the species to be detected [104]. Polymeric composite matrices with CNT, based on poly-epichlorohydrin and poly-ether-ethane, were used with good results for the detection of toluene and octane vapors, but they did not provide a sensing signal for light gases such as hydrogen, ammonia, nitrogen dioxide, and carbon monoxide [105]. Other composite matrices showed similar behavior, having good results for octane vapors, but without a signal for the same lower molecular mass gas molecules [106]. For quantitative and qualitative measurement of gases with
low molecular mass, the direct deposition of single-wall carbon nanotubes (SWCNT) has yielded much better results compared to other types of nanotubes [107].

Carbon nanotubes decorated or doped with metal metals/metal oxides have also shown good results in use when obtaining different sensors [108]. Thus, CNTs decorated with cerium oxide were used for the detection of acetone and ethanol in the mixture [109], CNT decorated with ZnO-CuO for the detection of iso propanol vapor at room temperature [110], SWCNT decorated with Cu nanoparticles for hydrogen sulfide detection [111], CNT decorated with gold and silver complexes for the mixture of acetones, chloroform, ethanol, and humidity [112]. There is a small number of applications reported in the field of SAW structure-based biosensors with CNT due to the limitations given by obtaining a matrix homogeneous enough in order to obtain a sensitive one. However, solidly mounted resonators with a CNT coating that act both as an electrode and sensing layer have been reported as a gravimetric biosensor [113].

Different deposition methods have been used over time for obtaining sensor structures, the most modern referring to the synthesis of different inks for both the electrode component and the dispersion of CNT. We will discuss some examples in the next section.

In addition to carbon nanotubes, the potential of graphene was exploited for obtaining matrices for the SAW-based sensor structure. Originally used as filler for different polymer matrices [114–119], the start of these in the field of sensors was justified by high electronic conductivity on the surface, which was much higher than in the case of carbon nanotubes, as well as the versatility of multiple functionalization and derivatization reactions and countless possibilities of deposition on electronic structures. Most of the research reported so far on graphene-based SAW sensors [120–123] has the same applications as those based on carbon nanotubes, the difference being given by the much higher sensitivity in the case of graphene, due to better adhesion to the substrate. Applications cover humidity detection [124–127], hydrogen [128,129], ammonia [130], nitrogen oxide [131,132], or carbon dioxide [133]. Modern applications refer to the detection of combat gases [134] for both authorities and soldiers during conflicts.

Very recently, a structure based on a thin-film transistor configuration with carbon nanotubes as the channel material aiming at electrically tunable SAW propagation has been demonstrated, thus opening a venue for next generation SAW-based devices [135]. The quantitative characteristics for some of the presented matrices are summarized in Table 2.

Table 2. Quantitative characteristics for different SAW sensors based on carbon nanotubes active materials.

| No | Sensitive Layer | Detected Species | Sensitivity | Reference |
|----|-----------------|------------------|-------------|-----------|
| 1. | MWNTs/polyethylene imine | CO₂ | 0.5–100% in air | [101] |
| 2. | Poly(diallyldimethylammonium chloride)/SWCNT | CO₂ | 0–10% in air | [103] |
| 3. | Polyepichlorohydrin/polyetherurethane/MWNT | Octane | 0.59–1.01 Hz/ppm | [105] |
| 4. | Polyepichlorohydrin/polyetherurethane/MWNT | Toluene | 0.61–4.38 Hz/ppm | [105] |
| 5. | Polyisobutylene/MWNT | Octane | 4.596–7.034 Hz/ppm | [106] |
| 6. | Polyisobutylene/MWNT | Toluene | 2.016–3.002 Hz/ppm | [106] |
| 7. | SWCNT Langmuir–Blodgett film | H₂ | 0.030–1% | [107] |
| 8. | SWCNT Langmuir–Blodgett film | NH₃ | 30–1000 ppm | [107] |
| 9. | SWCNT Langmuir–Blodgett film | NO₂ | 1–10 ppm | [107] |
| 10. | ZnO–CuO/SWCNT | 2-propanol | 200.26 kHz/100 ppm | [110] |
| 11. | ZnO–CuO/SWCNT | Trichloromethane | 59.8 kHz/100 ppm | [110] |
| 12. | ZnO–CuO/SWCNT | Dichloromethane | 33.42 kHz/100 ppm | [110] |
Table 2. Cont.

| No | Sensitive Layer            | Detected Species | Sensitivity          | Reference |
|----|----------------------------|------------------|----------------------|-----------|
| 13 | ZnO–CuO/SWCNT             | n-Hexane         | 30.76 kHz/100 ppm    | [110]     |
| 14 | ZnO–CuO/SWCNT             | n-Pentane        | 10.89 kHz/100 ppm    | [110]     |
| 15 | ZnO–CuO/SWCNT             | Diethylether     | 89.46 kHz/100 ppm    | [110]     |
| 16 | ZnO–CuO/SWCNT             | Acetone          | 107.23 kHz/100 ppm   | [110]     |
| 17 | ZnO–CuO/SWCNT             | Acetonitrile     | 10.64 kHz/100 ppm    | [110]     |
| 18 | ZnO–CuO/SWCNT             | Ethanol          | 100.69 kHz/100 ppm   | [110]     |
| 19 | ZnO–CuO/SWCNT             | Methanol         | 20.99 kHz/100 ppm    | [110]     |
| 20 | Cu nanoparticles/SWCNT    | H₂S              | 5–200 ppm            | [111]     |

3. Coating Techniques of SAW Sensors

Many reports on the development of SAW devices used to analyze toxic and chemical species are available; however, many of these reports raise the issue of inconsistency when depositing the active chemical interactive membrane (CIM) onto the SAW devices. Taking into account the constraints generated by the ability of the SAW resonators to respond to the physical changes in the overlaying active CIM, for example mass or viscosity changes, it is most important to control the thickness, roughness, and placing of the active CIM.

In this section, we present some of the coating techniques for the chemical interactive membranes in SAW devices, which are prompted by criteria such as miniaturization (for example thickness, lateral dimension) and simplicity of processing. A short overview of the coating methods for SAW devices is given in Figure 4.

![Figure 4. Scheme of the coatings methods used in acoustic devices.](image-url)

Spin coating, spray coating, and ink jet printing are the most common methods for the “direct writing” of polymers to the surface of SAW devices. Below, we will present a short overview of these three techniques, and a comparison of these techniques is shown in Table 3.
### Table 3. Comparison of “direct writing” techniques for the application of active coatings in SAW devices.

| Coating Technique | Coating Materials | Velocity of Transfer Material | Cost | Problems |
|-------------------|-------------------|-------------------------------|------|----------|
| Spray coating     | Wide range of materials (metal, alloy, plastic, polymer, etc.) | 450–1000 m s\(^{-1}\), depending on the spray device, spray material, and operating conditions | Inexpensive | Finish quality |
| Inkjet printing   | Specially designed inks | 1–5 m s\(^{-1}\) | Inexpensive | Properties of the liquid limited ink types |
| LIFT              | Can work for all types of material phases | From 2000 m s\(^{-1}\) (gold particles) to 100 m s\(^{-1}\) (flyer material) | Moderately expensive; requires laser, works also in air | UV and thermal load; Preparation of multilayer donor |
| MAPLE direct write| Polymers material is embedded in a matrix | 200 m s\(^{-1}\) | Expensive; requires vacuum | UV and thermal load; Preparation of the matrix |

#### 3.1. Spin Coating

Spin coating is a widely used technique for the deposition of thin films, offering a high degree of reproducibility [18]. The process relies on pipetting a small volume of a fluid (a polymer dissolved in a compatible solvent) onto a spinning substrate. Centripetal acceleration will cause most fluids to disperse, leaving a thin polymer film on the surface. The final film thickness will depend on the fluid’s viscosity, drying rate, percent of the solid in the solution, surface tension, etc. as well as on the parameters chosen for the spinning process.

In [69], Joo et al. reported on SAW sensors coated with different polymers (i.e., polyisobutylene (PIB), polyepichlorhydrine (PCH), polydimethylsiloxane (PDMS), polybutadiene (PBD)) by spin coating and the investigation of their sensing properties toward different chemical agents such as dimethylmethylphosphonate (DMMP) and dichloromethane (DCP). They obtained frequency shifts of 5.369 kHz in the case of a PIB-coated SAW sensor when exposed to 5 ppm DMMP, while in the case of a PIB film, the frequency shift was around –3.527 kHz when exposed to 5 ppm of DCP. These results proved a good selectivity to stimulant gases, suggesting that it is possible to apply the SAW devices coated by spin coating with different polymers for the detection of chemical warfare agents.

However, the spin coating process presents some disadvantages, i.e., the lack of material efficiency. Generally, the spin coating process uses 2–5% of the material pipetted onto the substrate [136], while the remaining 95–98% is spread into the dispensing vessel. Another disadvantage is the decreased throughput; i.e., large substrates cannot be coated at a sufficiently high rate in order to allow the film to thin and dry in a timely manner.

#### 3.2. Spray Coating

Another technique for applying active layers in SAW sensors is spray coating. In this method, a fluid under high pressure is sprayed at a high speed through a nozzle. The friction between the fluid and the air breaks the fluid into fragments and ultimately into droplets. One of the advantages of this technique is that it offers a high production rate.

An example of a functional SAW device coated by this technique is reported in [137], where an SAW electronic nose with different polymers as CIMs was developed to differentiate between wines of the same variety of grapes from the same cellar. The authors applied principal component analysis and showed that the SAWs could discriminate among the different wines. In addition, the classification by probabilistic neuronal network showed a 95% success rate.

However, the main disadvantage is the limited control over the finish quality [138]. Even more, spray coating is associated with macro-molecule “bubbles” at the polymer–SAW substrate interface [20,139,140].
3.3. Inkjet Printing

Inkjet printing is an additive manufacturing method that provides a flexible and cost-effective microfabrication technology. This non-contact technology can be used for printing a wide range of liquids including polymers, proteins, or nanoparticle-containing solutions onto different substrates, rigid or flexible, rough or smooth. Inkjet printing allows the printing of active layers in SAW sensors and also interdigital transducers [141,142].

The advantages of this technique are the accuracy, high resolution, high speed, and little consumption of material as compared to a lithographic process [143]. These advantages make this technique an appropriate tool for precisely positioning the coatings onto SAW devices [144]. One of the most important disadvantages of inkjet printing is clogging of the print heads.

For example, in [145], the authors have reported on inkjet printing of graphene oxide layer-by-layer for the fabrication of Love wave devices. They could prove that the GO SAW sensors show sensitivities of 30 Hz/ppm, 24 Hz/ppm, and 2.4 kHz/1% for C$_2$H$_4$O, C$_7$H$_8$, and relative humidity, respectively.

3.4. Laser-Based Methods

Ever since the first generation of laser light in 1960, the use of lasers is far reaching and prevalent from manufacturing to medicine in surgeries, microfabrication, security, lighting, displays, and nanotechnology, just to name a few.

Pulsed laser deposition (PLD) is the most used technique for the deposition of various materials as thin films.

Briefly, in PLD, a laser beam interacts with a solid or liquid target, resulting in a plume that is transporting the ablated species to a substrate, where a thin film is formed. A scheme of the PLD working principle is shown in Figure 5a [146].

![Figure 5](image)

Figure 5. Schematic representation of the (a) pulsed laser deposition (PLD) and (b) MAPLE experimental setups.

Early works on PLD of oxide and nitrate (for example AlN, ZnO, or LiNbO$_3$) thin films aiming at applications in SAW devices have been mainly focused on the deposition, characterization, and optimization of the deposited layers [147–150]. Principally, the researchers have focused on tuning the structure, composition, and morphology of the piezoelectric material thin films. The requirements for the development of functional SAW devices are smooth surfaces in order to prevent scattering of the propagating surface acoustic waves [72].

More recently, the deposition of Pd/ZnO bilayers, TiO$_2$ monolayers, Pd/TiO$_2$ bilayers, ZnO nanowires and thin films, or dense Pd/WO$_3$ bilayers by PLD which were applied as active coatings in SAW devices has been reported in [32,151–154]. The as-fabricated SAW sensors have shown promising results for the detection of hydrogen at room temperature.

However, due to the fact that pulsed laser deposition may photochemically or thermally damage the soft materials as for example the polymers or biocompounds, a gentle
approach derived from PLD has been developed [155,156]. This approach, i.e., matrix assisted pulsed laser evaporation (MAPLE), is similar to the PLD method, with a different procedure for target fabrication. The target in MAPLE (see Figure 5b) for the schematic representation) consists in the material of interest being suspended/dissolved in a compatible solvent at concentrations of 0.1–5 wt % or v/v% and flash frozen with liquid nitrogen. The laser beam is focused or imaged on the resulting solid target, the solvent is evaporated during the process, and the material of interest is collected onto a substrate placed parallel and in proximity (3–5 cm) to the target.

Over the years, MAPLE has been successfully used in SAW sensor applications [60,156–158]. MAPLE has been used for the deposition of various chemoselective polymers, such as a fluoroalcoholpolysiloxane polymer (SXFA) [159], polyisobutylene, polyethylenimine [78,156], polyepichlorhydrine [78], etc. Another example is focused on the deposition of fluoropolyol, a sorbent chemoselective polymer, as thin film by resonant infrared pulsed laser deposition (RIR-PLD) using a free electron laser operating at 2.90 µm [158], and [159] demonstrates the deposition of polysiloxane thin films with applications in chemical sensors.

The PLD and MAPLE techniques presented above are appropriate for the deposition of coatings with controlled thickness and roughness on different types of substrates. However, for direct patterning or high resolution “writing” of substrates with different phased materials, i.e., solids, liquids, viscous pastes, ink-containing suspensions, etc., alternative approaches are needed. One of the laser-based approaches is laser-induced forward transfer (LIFT) [160].

In LIFT, a laser beam is used to transfer material “pixels” from a donor support to a receiver substrate. The laser beam is either focused or imaged at the transparent donor support–material to transfer interface, and by each laser pulse, a material “pixel” is “written” onto the receiver substrate. The receiver substrate is placed parallel and at a short distance (generally few micrometers for solid layers and a couple of hundred micrometers for liquid layers) from the donor support.

Since its development [160–164], it has been used for the transfer of a wide range of materials and also functional devices [165]. Here, we will only present a few examples of functional SAW sensors where the active materials have been applied by LIFT. A scheme presenting the LIFT method used for the application of active materials in SAW sensors is shown in Figure 6.

![Figure 6](image.jpg)

Figure 6. Schematic description of the LIFT method applied to transfer the active materials (polymers) directly onto SAW devices.

A modified version of LIFT, i.e., where an intermediate triazene polymer layer is added, has been used for the development of chemical sensors for the detection of volatile organic compounds (VOCs) and warfare agents. The intermediate layer has the role of protecting the material to transfer from thermal damage and also to provide sufficient
thrust to propel the material of interest. This modified LIFT is named dynamic release layer (DRL)-assisted LIFT.

By DRL–LIFT, different functional devices have been reported, i.e., SAW resonators, solidly mounted resonators (SMR), or delay line [160]. For example, SMR devices printed by DRL–LIFT have been reported in [165]. A scheme of an SAW–SMR device together with devices printed by LIFT is shown in Figure 7a,b.

![Figure 7. (a) Scheme of a SAW–SMR device. (b) Optical microscopy images of SAW–SMR devices with PEI pixels transferred at (left) 400 mJ/cm² and (right) 300 mJ/cm² laser fluence. (c) Real-time response of the PEI-coated SMR sensor for different concentrations of DMMP. (Reproduced with permission from [165], Copyright 2021, ELSEVIER).](image)

Polyisobutylene (PIB), polyethylenimine (PEI), and polyepichlorhydrine (PECH) pixels were printed on the active area of the SAW–SMR devices, and then, the sensitivity, resolution, and response time to dimethyl methylphosphonate (DMMP) was evaluated.

It has been found that following the exposure to various concentrations of DMMP (i.e., between 22 and 127 ppm), the SAW–SMR sensors present fast and reversible responses, PEI coated SAW–SMRs being the most sensitive, followed by PIB and PECH. An example of a real-time measurement against different concentrations of DMMP is shown in Figure 7c [165].

Other examples of functional SAW devices are reported in [72,73], where arrays for the detection of volatile compounds based on surface acoustic wave resonators coated with different polymers (i.e., polyepichlorohydrin, polyisobutylene, polyethyleneimine, (hydroxypropyl)methyl cellulose, and poly(styrene-co-maleic acid) partial isobutyl/methyl mixed ester) are presented.

In particular, in [73], two successive laser-based methods were applied for the application of the active coating in the SAW resonators. First, matrix-assisted pulsed laser evaporation was used to deposit the thin polymer layers, followed by LIFT to pattern the polymer pixels directly onto the SAW resonators. The SAW resonators were tested upon exposure to different concentration of ethyl acetate, dimethyl methylphosphonate, dichloromethane, dichloropentane, and water. The SAW resonators showed different sensitivities to the selected chemicals, and even more, they could discriminate between the vapors considered. An example of SAW resonators printed by LIFT together with the sensitivities exhibited by the sensors and the biplots of loadings and scores of the principal component analysis and is shown in Figure 8 [73].
Vapors considered. An example of SAW resonators printed by LIFT together with the sensitivities exhibited by the sensors and the biplots of loadings and scores of the principal component analysis is shown in Figure 8 [73].

Figure 8. (a) Optical microscopy images of the SAW resonators printed by LIFT at different laser fluences. Scale bar is 400 µm. (b) The sensitivities of the SAW resonators coated by LIFT to the different vapors tested. (c) Biplots of loadings and scores of PCA using the first two principal components for the SAW resonators coated by LIFT. (Reproduced with permission from [73], Copyright 2021, ELSEVIER).

Not only solid polymer thin films can be printed by LIFT, but also liquid protein thin films may be used as donor materials. When using a liquid thin film as the donor material, generally glycerol is added, with the purpose of preventing the solution from drying out. An example is shown in [166–168], where SAW biosensors for odor detection in the food industry are reported. The SAW biosensors are coated by LIFT with different bovine odorant binding protein (OBP) solutions containing 20% and 50% glycerol. Three different OBP solutions were printed, i.e., wild-type OBP from bovine, a double-mutant of the OBP from bovine (dmbOBP), and the wild-type OBP from pig (wtpOBP) with the purpose of fabricating a SAW array aiming at the detection of R-(−)-1-octen-3-ol (octenol) and R-(−)-carvone (carvone) vapors.

An optical microscopy image is shown in Figure 9a of an SAW device coated by LIFT with a liquid thin film containing 20% glycerol. The uniform coating is formed out of overlapping droplets of approximately 60 µm in diameter printed with an overlap of 40 µm. When testing the functionality of the as-deposited SAW devices against different concentrations of octenol and carvone, high sensitivities were obtained (i.e., 0.48 ppm for the detection of octenol and 0.74 ppm for the detection of carvone), and the detection limit was in the low ppm range. Moreover, as it can be seen from Figure 9e, the LIFT-fabricated OBP-based biosensor can discriminate the octenol molecules from the carvone molecules. These are promising results, which open up new venues for the application of laser-based methods for the development of novel biosensor-based systems.
Figure 9. (a) Optical microscopy image of a SAW resonator coated with an OBP solution containing 20% glycerol, at a laser fluence of 650 mJ/cm²; (b) Sensitivity of the wtbOBP, dmbOBP, and wtpOBP-based biosensors upon exposure to different concentrations of octenol and carvone; Responses of the OBPs biosensors to different concentrations of (c) Octenol; (d) Carvone; (e) Biplot of loadings and scores using the first two principle components of the PCA analysis. (Adopted with permission from [167,168], Copyright year 2021 ELSEVIER).

4. Conclusions and Future Perspectives

The latest technological advances are directed toward the integration of smart materials, novel material processing techniques, and sophisticated electronics onto systems dedicated to the improvement of life quality and creating safer environments. Surface acoustic wave (SAW) sensor devices are clear examples of sensor systems that benefit from these technological advances. Nowadays, researchers are focusing their efforts into combining “smart” thin film materials with specific sensor designs and signal processing techniques in order to achieve competitive SAW sensor systems.

In this review paper, we have focused on presenting the latest progress in polymers and functionalized carbonaceous materials for applications as recognizing elements in SAW sensors followed by different coating techniques for SAW sensors.

There are many efforts dedicated to the improvement of SAW sensors by the development of new and improved sensitive materials and coatings for SAW devices, for example, either increasing the specificity of polymers toward a given analyte by molecular tailoring or surface tunability. Not only can the morphology (roughness over different thicknesses) of the coating be adjusted over a wide range, but the polymers can also be functionalized to become chemically sensitive to adsorbates.

In addition, the detection limit, as well as the sensitivity of the SAW sensors is influenced by the chemical nature and the concentration of the sensor sensitive material coating. Both parameters influence the sorption–desorption mechanisms and the elasticity of the sensory coating. Surface adsorption mechanisms are usually based on the chemical affinity of the species to be detected for substrate with weak chemical interactions formation (ionic, van der Waals, coordination or hydrogen bonds), in very rare cases with the formation of covalent bonds. The formation of covalent bonds would lead to a much higher sensitivity but would have consequences on the regeneration of the matrix and the inability of the sensors to function over several measurement cycles (basically, it would obtain sensors for a single detection). The formation of covalent bonds would also ensure much higher specificity than at this time. In the case of sensors on SAW type architecture, specificity is a practical problem, which is why the commercial value is currently low compared to other types of sensors.

In the particular case of carbon nanotubes, a detection mechanism based on the non-covalent interaction between the surface of a non-functionalized carbon nanotube cannot
provide specificity as long as a wide range of chemical species can interact with that surface: cations, vapors of volatile organic compounds, water vapors, gases. Furthermore, another limitation of these sensors is that chemical species with high molecular mass cannot be determined, because the loading on the sensor coating would be too high, with the impossibility of applying the principle on which these sensors operate.

While the SAW sensors based on polymers and CNTs for chemical sensing are very common; largely, studies and approaches for graphene-based SAW sensors and biosensors are still inadequately represented. For example, the use of graphene as a sensing material in SAW biosensors represents a medium- and long-term challenge. Covalent immobilization (for a more stable matrix) of specific antibodies for a particular tumor marker will open up the possibility of obtaining and manufacturing biosensors with specific responses, practically for any medical condition or disease that is characterized by the release into the blood of markers. Another area that will know a special development refers to sensors with military applications, especially those ‘wearable’ both for the detection of substances used in conflicts, as well as for monitoring the biological parameters of soldiers.

In addition, there are numerous coatings methods for SAW devices in order to achieve successful analysis of different gases and liquids. These methods range from very simple and cost effective, such as drop casting or spray coating, to more complicated such as atomic layer deposition or electropolymerization. Owing to the need for more sensitive, selective, and more cost-effective SAW sensors, laser-based methods have the opportunity to become major players in the field. In particular, of the laser-based coating methods for active sensing layers, laser-induced forward transfer shows the most promise for a rapid and cost-effective patterning of the SAWs.

To sum up, taking into account the developments in materials science as well as the advances in novel technologies, the field of surface acoustic wave sensors is expected to grow continuously.

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